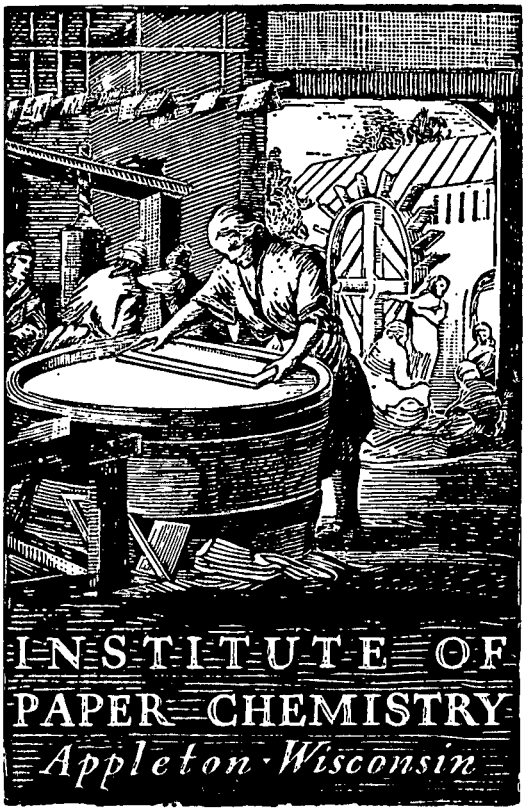

IMPROVED PROCESS FOR BLEACHED CHEMICAL PULPS NONCHLORINE BLEACHING

Project 3474-2

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

October 17, 1980

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The study of the effects of oxygen derived radicals on the degradation of pulp began with a consideration of the action of KO_2 (a source of the superoxide radical-anion) in aprotic solvent on a variety of pulps and model substances. The latter studies indicated KO_2 reacts readily with both carbohydrates and lignin. This behavior was confirmed when pulps were reacted and it was further noticed that the extent of reaction (loss of yield) depended on the rate of sample shaking. This behavior is probably due to both mixing and chemical activation promoted by the treatment. The fibers were also cleaved into smaller fragments by the action of KO_2 and mechanical treatments. It was postulated that this reaction was enhanced by the stresses produced by mechanical flexing of fibers. Since all the reactions occur in both dimethyl sulfoxide (DMSO) and pyridine solvents, the reactive intermediates thought to occur in mixtures of DMSO and KO_2 do not participate in these reactions. The rapid loss of pulp viscosity contrasted to the slower loss of yield during the reactions suggests penetration factors may influence pulp yield, whereas the degradation of viscose fibers without appreciable yield loss indicate mechanical stresses are necessary for fiber cleavage.

Although these reactions were carried out in a nonaqueous system, the mechanisms of cellulose and fibrillar cleavage encountered here may have a bearing on the change in strength properties after oxygen pulping. The tendency for yield loss even with gentle shaking may be related to changes in yield and in beating properties after oxygen treatments. The degradations may become a tool for understanding the changes in fiber structure caused by beating and

refining and will certainly become a tool for studying the structure of tracheids and natural and synthetic fibers.

Preliminary results are presented on experiments designed to determine the effects of oxygen-derived radicals on pulps in aqueous media. A technique for attempting to bleach pulp with singlet oxygen was developed, and significant brightening was achieved in short reaction times. It is not known whether the bleaching action was the result of the action of singlet oxygen or whether some other reagent also contributed to the brightening. The nature of some of the reactive species will be determined using chemicals known to react with radicals in predetermined ways. Gas chromatographic (GLC) techniques for the analysis of certain of these compounds have been developed, and control oxidations to verify their behavior in the literature have been begun. Techniques for the analysis of the oxidation products by GLC-mass spectroscopy are under development.

INTRODUCTION

The objective of this project is to investigate the potential chemical difficulties of a nonchlorine bleaching system based upon the use of oxygen-derived chemicals with the hope of improving the commercial utility of such processes. Many of these chemicals, such as peroxide, ozone, oxygen, and other closely related compounds, can produce similar powerful degradation products such as hydroxyl radical, singlet oxygen and superoxide radical. This project proposes to examine the degradative action of these common harmful intermediates upon pulp fibers for the ultimate purpose of minimizing their harmful effects and maximizing their beneficial actions during bleaching.

As discussed in previous reports (1) and interim reports (2) it was planned to react pulp with the various radicals mentioned above to determine their effects on pulp properties, and to attempt to detect these radicals during oxygen and peroxide bleaching sequences. For experience, pulp was first reacted with superoxide in nonaqueous solution although it was recognized that this did not represent a model of actual bleaching technology.

This report summarizes and brings to completion the initial research reported in the interim reports (2) on the action of superoxide with pulp. The treatment is longer than anticipated because of the discovery of previously unreported degradative phenomena. Also included are the initial experiments directed toward the immediate goals of the project.

It was not anticipated that the reaction of pulp with KO_2 in an anhydrous medium would lead to excessive pulp degradation although the existence of secondary degradations from peroxide, hydroxide ion and oxygen might be evident.

This behavior was anticipated from a review of the chemical activity of superoxide reported in the literature (3).

Because of its limited solubility and the lack of good analytical techniques, the chemical action of superoxide has not been extensively studied until recently. It has some solubility in dimethyl sulfoxide (DMSO) which can be increased further by the use of 18-crown ether. In the presence of crown ether, the basicity of $\cdot O_2^-$ would become more apparent by removing a proton from substrates and solvents (4). The equilibrium

$$H^+ + \cdot O_2^- \rightleftharpoons HO_2^\cdot \qquad pK_a = 4.77 \tag{1}$$

indicates that superoxide ion in solutions can promote proton transfer from substrates to an extent equivalent to that of the conjugate base of an acid with a pK_a of about 23. Since the following reaction is rapid and highly exothermic, it has been argued that the lifetime of $HO_2^\cdot$ should be sufficiently short to preclude

$$\cdot O_2^- + HO_2^\cdot \rightarrow O_2 + HO_2^- \qquad k = 8.5 \times 10^7\ M^{-1}\ S^{-1} \tag{2}$$

it as a major reactant with most substrates (5).

Acids weaker than water will produce an exothermic reaction with $\cdot O_2^-$, but it has been argued that exceedingly weakly acidic compounds such as benzaldehyde do not react with it. The observed reactivity is thought due to the reaction of impurities with superoxide producing an anion [Eq. (3)] which leads to the degradation of benzaldehyde by a Cannizzaro-type reaction.

$$2\cdot O_2^- + HB \rightarrow O_2 + HO_2^- + B^- \tag{3}$$

In the presence of water or other proton sources, superoxide ion yields strong Bronsted bases. These processes produce peroxide and oxygen, and this combination of base and dismutation product is claimed to account for many of the reactivity characteristics that have been attributed to the superoxide ion itself.

Superoxide can undergo a nucleophilic attack on alkyl halides in aprotic solvents. Kinetic studies have shown the reaction rates to follow the order 1°>2°>3° for alkyl halides and tosylates, and the attack by superoxide ion results in inversion of configuration (6,7)

$$RX + \cdot O^- \rightarrow RO_2^{\bullet} + X^- \qquad (4)$$

$$RO_2^{\bullet} + \cdot O_2^- \rightarrow RO_2^- + O_2 \qquad (5)$$

$$RO_2^- + RX \rightarrow ROOR + X^- \qquad (6)$$

In the presence of DMSO, Eq. (5) may be followed by attack on solvents to yield alcohols and dimethyl sulfone (6,8,9). Radical traps have confirmed

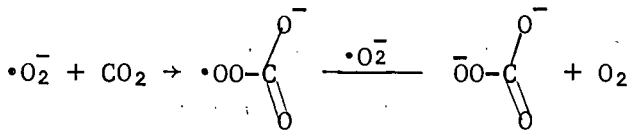
$$ROO^- + Me_2SO \rightarrow RO^- + Me_2SO_2 \qquad (7)$$

the existence of ROO. and RO. in many instances (10) but the nature of the solvent effects remains poorly understood.

Nucleophilic attack by superoxide ion on esters yields acids and alcohols (11,12). It has been shown that acyl oxygen scission occurs by noting the complete retention of configuration in the alcohol moiety from an optically active ester.

$$\cdot O_2^- + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR_1 \rightarrow R\text{-}\overset{O^{\ominus}}{\underset{OO\cdot}{\overset{|}{C}}}\text{-}OR_1 \xrightarrow{RCHO} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^- + R\,CH_2OH \qquad (8)$$

A recent observation (13,14) is that a combination of $\cdot O_2^-$ and CO_2 in aprotic media results in $CO_4^=$ formation probably by the following mechanism.



$$\cdot O_2^- + CO_2 \rightarrow \cdot OO\text{-}C(=O)(O^-) \xrightarrow{\cdot O_2^-} {}^-OO\text{-}C(=O)(O^-) + O_2 \qquad (9)$$

Superoxide is able to act as a moderate reducing agent in aprotic solvents by donating one electron (15). A recent study has shown that superoxide ion reduces sulfur dioxide to dithionite in dimethyl formamide. A conflict of opinion exists in the literature as to whether the reaction of superoxide with alkyl hydroperoxides is an example of reductive cleavage of the O-O bond (16,17,18) or whether the hydroperoxide serves primarily as a proton source to bring about the rapid transmutation of $\cdot O_2$. Another proposed reduction by $\cdot O_2^-$ is the quenching of singlet oxygen (19). A closely

$$^1O_2 + \cdot O_2^- \rightarrow \cdot O_2^- + {}^3O_2 \quad \Delta G = -91kJ, \; k = 1.6 \times 10^9 \; M^{-1} \; s^{-1} \qquad (10)$$

related and as yet unresolved problem is whether singlet or triplet oxygen results from the oxidation and transmutation of superoxide radical anion. Some experiments indicate catalytic influences have a profund influence on the production of this product (20,21). Other recent research is directed to the ability of superoxide to complex with metals in various media including aqueous media and DMSO (22-27).

In summary, the oxidative inertness of superoxide is suggested by its nonreactivity with a wide variety of functional groups under rigorous aprotic conditions. In the presence of proton sources, superoxide dismutates rapidly to peroxide and water. A reasonable explanation for observed oxidation reactions involving $\cdot O_2^-$ is that they actually involve intermediates and products of the

proton-induced dismutation reactions. It was anticipated therefore that the reaction of pulp (thoroughly solvent-exchanged into DMSO or pyridine) with superoxide would be no more drastic than a corresponding reaction of the pulp with peroxide in DMSO or pyridine.

RESULTS

INITIAL EXPERIMENTS

A simple experimental technique was adopted for this initial investigation which involves the use of a Teflon-sealed 125 mL narrow necked bottle (shown in Fig. 1) and a Kahn shaker to ensure good mixing of the dissolving superoxide. Standard shaking conditions operated at 232 beats per minute at room temperature. Slower shaking rates and other shaking devices were employed later in the investigation.

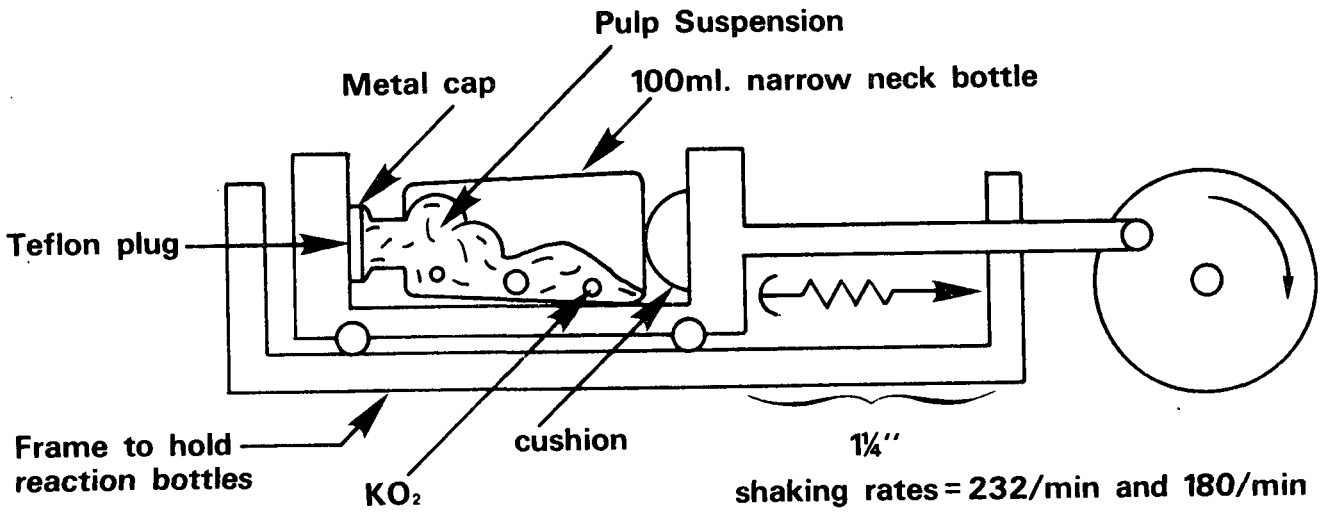
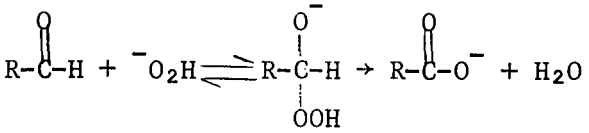


Figure 1. Schematic Diagram of Superoxide Reactor

The solubility of KO_2 in DMSO was found to be about 35 mM at room temperature and that of pyridine at about 5 mM. The exact value is somewhat uncertain as the superoxide decomposed slowly to peroxide and these components could not be distinguished readily from one another by the iodine test used for analysis. Although 18-crown ether increased the solubility of KO_2 greatly in

both DMSO and pyridine, it participated in the reactions, and since it caused the formation of a white explosive precipitate, its use was abandoned.

Cellobiose was found to react very quickly with KO_2 in both DMSO and pyridine. Its half life in the former solvent was 30 minutes at room temperature with an apparent first order dependence on cellobiose concentration. Examination of the reaction products by gas chromatography (GLC) showed glucosylarabinonic acid to be the major product when DMSO was solvent and cellobionic acid to be the major product when pyridine was the solvent. According to the literature, the reactivity must be due to the participation of impurities such as water in the reaction. It was felt the rapidity of degradation was not consistent with the known behavior of aldoses to dilute peroxides and that the speculations in the literature should be questioned. The difference in reaction products between pyridine and DMSO solvents was not unexpected in view of the solvent effects of DMSO reported in the literature (28,29). The degradation of cellobiose in pyridine may be represented as follows:



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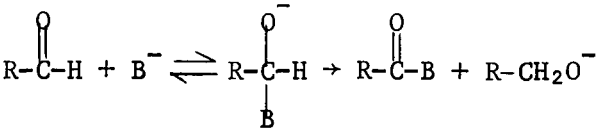

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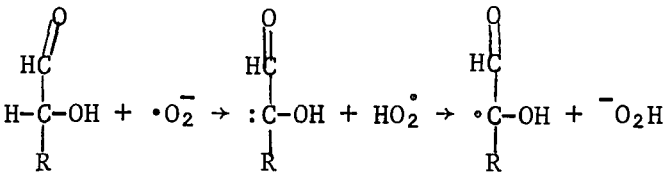
The detection of glucosylarabinonic acid (as well as cellobionic acid) in the reaction employing DMSO as solvent may be related to the well known enhanced reactivity of bases in DMSO. The following sequence of reactions can be imagined



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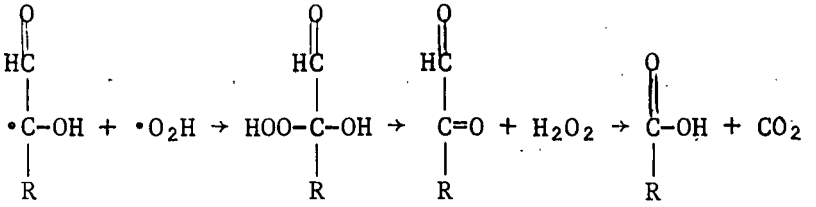
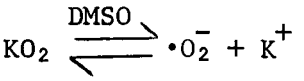


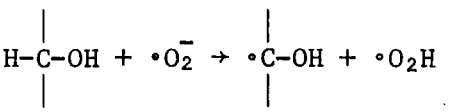
(14)

to occur in addition to those that occur in the presence of pyridine.

Methyl β-D-glucopyranoside (MBG) reacted at a slower empirical rate than cellobiose (half life: 4 hours at room temperature, 90 minutes at 75°C) and exhibited an apparent zero-order dependence upon MBG concentration. This behavior does not reflect the rate of solution of KO_2 in DMSO but probably reflects the rate of formation of the carbenyl radical as follows:



(15)



(16)

These speculations were not investigated in this project but will be considered possible topics for academic research.

In summary, KO_2 reacts quickly with aldehydic groups and with glucosides by dissimilar mechanisms. The solvent affects the degradation of reducing groups probably by enhancing the basic character of the model and thus provides alternative sites for attack. It may affect the degradation of glycosidic bonds as well. Since degradation occurs in both pyridine and DMSO, the reactivity of KO_2 is not due to the conjectured interaction of KO_2 with DMSO to produce especially reactive intermediates. A slow reaction of KO_2 with DMSO was observed to produce a product suspected to be dimethyl sulfone. Interaction between KO_2 in an aprotic solvent and polysaccharide components of pulps is therefore to be expected.

THE EFFECT OF SUPEROXIDE ON PULP YIELD

The pulps employed in this investigation were laboratory-prepared southern pine kraft pulps of 19, 35, 39, 55 and 95 kappa and two different laboratory-prepared spruce kraft pulps of 16 kappa. Holocelluloses were also investigated and were prepared from small blocks of wood by a conventional technique (30); they were fiberized by gentle disintegration in 0.1N NaOH, were neutralized with acetic acid, and they were washed free of salts with water. As they had been prepared over a period of years, the holocelluloses had been preserved in the frozen state until needed. Viscose staple and 1/4 inch cotton staple (kindly provided by Mr. G. L. Louis, USDA, Southern Regional Research Center, New Orleans) were also employed. The latter sample was purified by conventional techniques employed in cotton technology (31). All fiber samples were carefully solvent-exchanged from water into anhydrous DMSO. The latter stages of the solvent exchange and subsequent manipulations were conducted in a dry box.

The limited solubility of KO_2 in DMSO and pyridine required the presence of excess reagent to overcome losses due to fiber consumption. Vigorous agitation on a Kahn shaker (1 1/4 inch strokes) ensured distribution of excess KO_2 into the fibrous suspension (1 gram at 1% consistency). The reaction was terminated with methanol containing 5% water since the use of pure water at this stage sometimes led to explosions. In most instances (as shown in Fig. 2) the last traces of DMSO and low molecular weight debris were removed with water, and the residues were solvent exchanged into methanol and air dried. Samples for analysis with the scanning electron microscope (SEM) were removed separately after the water wash and were isolated by critical point drying (CPD). In some instances, the water-soluble component was precipitated with a five-fold excess of methanol. The precipitate was isolated either by solvent exchange into ether and air drying or by

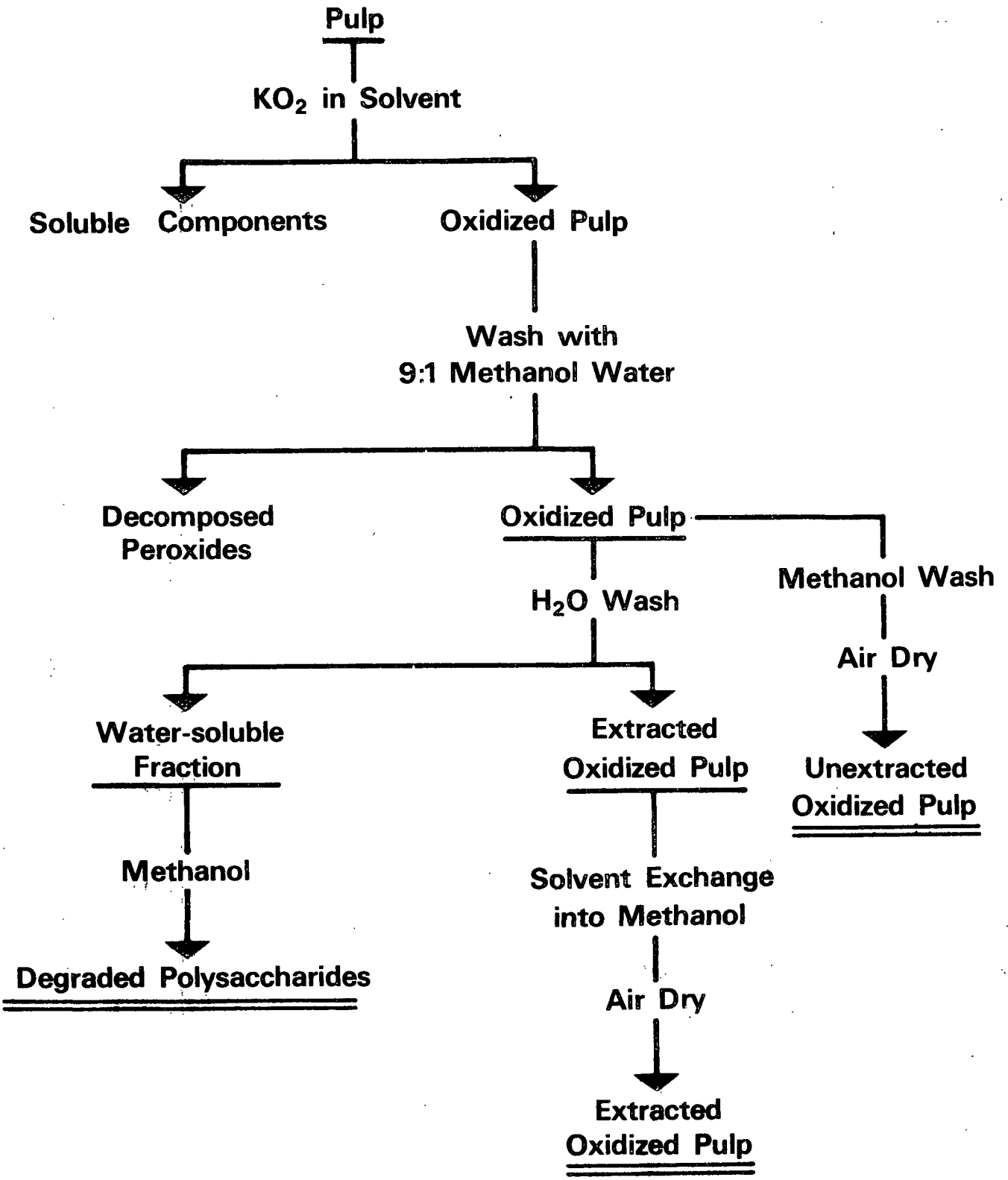


Figure 2. Flow Diagram for the Isolation of KO_2 Oxidation Products

freeze-drying from an aqueous solution. The change in yield was followed in all instances while sugar analyses, fiber length distributions, SEM light microscopic examination and characterization of the water soluble components was also carried out on selected reaction products.

The loss of yield with time of reaction was characterized by some variability and by the existence of induction periods. Nevertheless, the dependence of the extent of reaction on lignin content of a kraft pulp could be easily observed and was reported in a previous interim report (2). The plots in Fig. 3 show the effect of pulp kappa no. on the yield of laboratory-prepared kraft pulps after four hours reaction in DMSO at room temperature with standard shaking. The lower kappa (lower yield) pulp is the least adversely affected, and the most yield losses occur at intermediate lignin contents. This behavior to superoxide was confirmed when the response of a spruce kraft pulp (16 kappa) to KO_2 was diminished when the lignin content was reduced to a low level by sodium chlorite oxidation.

This relationship of oxidative action to lignin content is unexpected and demonstrates that the simple cause and effect response found after conventional bleaching practices is not observed here. The behavior can be associated with a multiple role of lignin in the reactions and/or to changes in fiber accessibility to KO_2 at different lignin levels. Lignin for example, can also act as a source of harmful radicals, if the critical oxidation potential of the functional groups in lignin is low enough (32). On the other hand, lignin is thought to behave as a terminator of radical reactions, and the properties of these two abilities may be related to the extent and types of pulping reaction. Lignin could also affect the interaction of superoxide with carbohydrate by acting as an incrustant and/or as a cross-linking component by preventing the penetration of the oxidant into the fiber wall. The mechanism of degradation in all likelihood does not involve peroxide

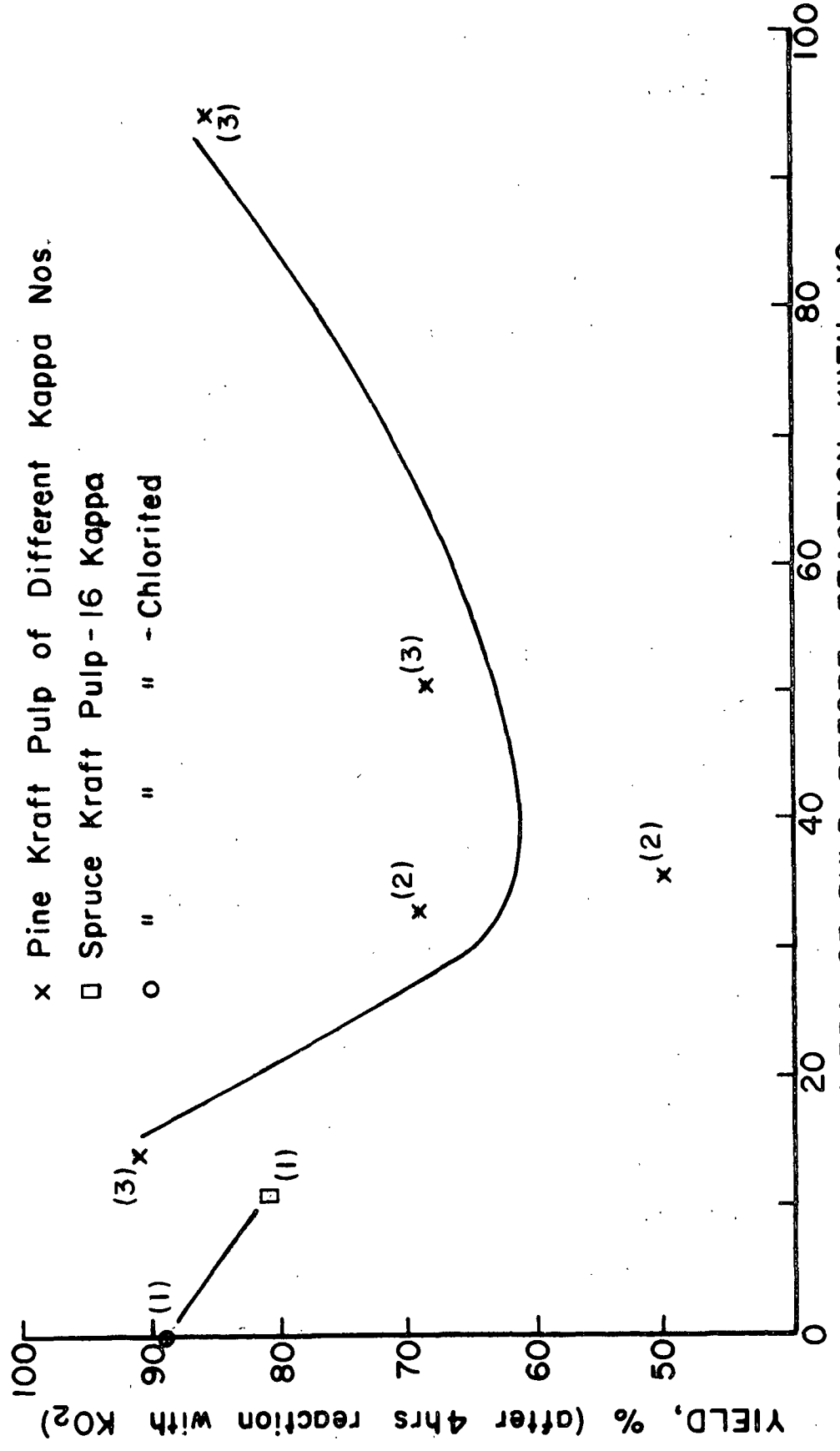


Figure 3. The Relationship Between Pulp Yield and Initial Kappa No. (Pulp Reacted With KO_2 in DMSO for 4 hours at Ambient Temperature)

intermediates as suggested by others since sodium peroxide in DMSO does not attack kraft pulp (Fig. 4).

Since the removal of lignin from a spruce kraft pulp with sodium chlorite resulted in increased resistance to oxidation (Fig. 3), it was anticipated that holocelluloses would also exhibit significant resistance to degradation by KO_2. The plots in Fig. 5 show that this is not the case. Holocelluloses can exhibit a wide range of responses ranging from the relatively inert incense cedar and pine compression wood to the more reactive amabalis fir holocellulose. The reasons for this behavior are not known, but they cannot be due to differences in mechanical damage because of the care taken in all instances to liberate tracheids. It is known that incense cedar has an unusual polysaccharide composition; the resistant tracheids in southern pine were latewood tracheids; and amabalis fir has very few latewood tracheids, whereas the pine compression wood holocellulose has anomolous chemical contents and fiber structures compared to normal tracheids.

The anomoly cannot be related to the presence of soluble lignin debris but may be related to the trace lignin still associated with the unextracted hemicellulose components. In another experiment, a southern pine thermomechanical pulp (TMP), prepared by Lyse (33), was reacted with KO_2 as shown in Fig. 6. The loss of yield was appreciable and would not have been predicted from the behavior of the 95-kappa southern pine kraft pulp described earlier.

The composition of some of the pulps and some of the water soluble extracts derived from them was analyzed by quantitative GLC analysis of their hydrolyzates. The results are recorded in Tables I and II and illustrative plots of the lignin and polysaccharide contents of the oxidation products from the 95 kappa southern pine kraft pulp are given in Fig. 7. The plots and the data

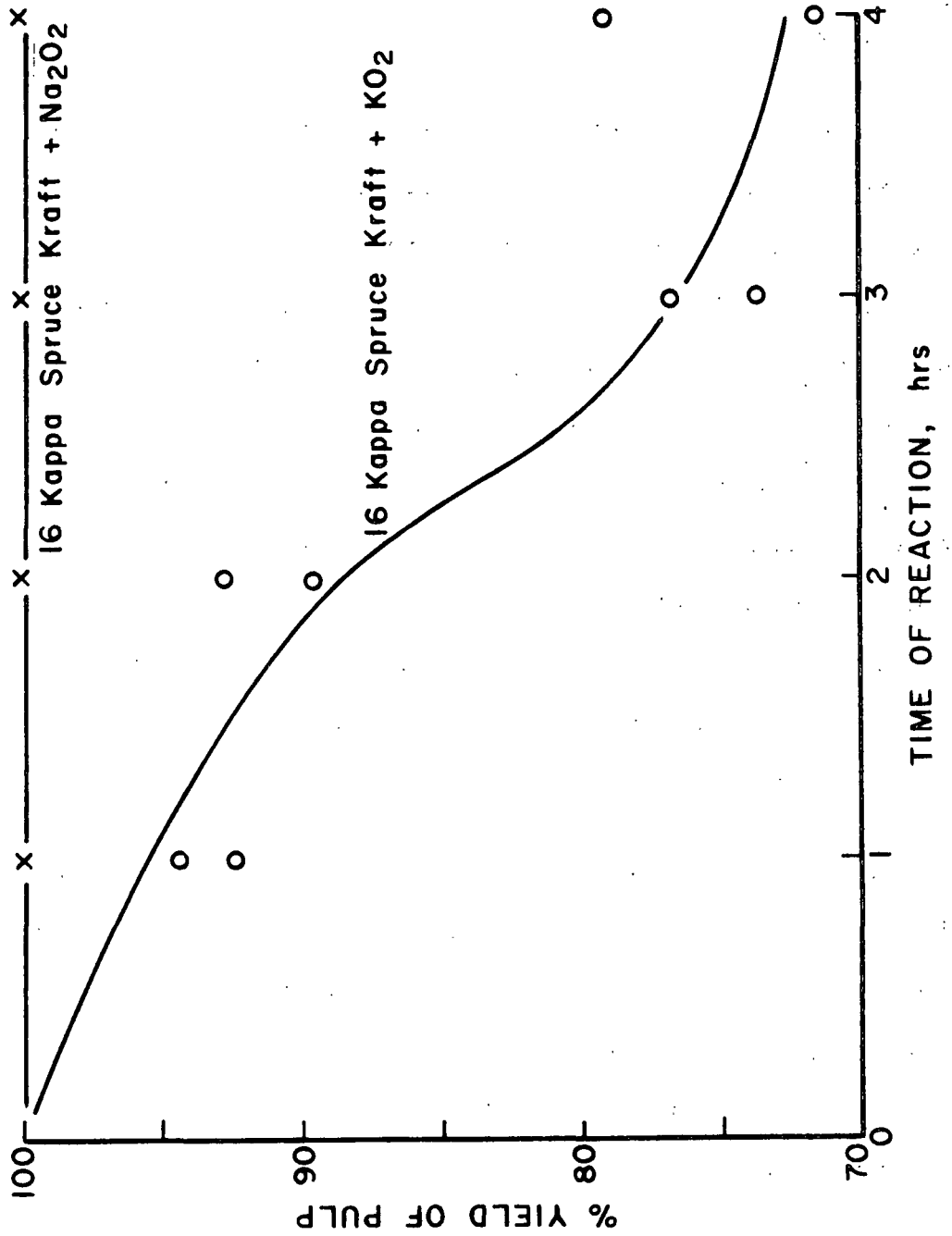


Figure 4. The Loss of Yield of Spruce Kraft Pulp When Reacted With KO_2 or Na_2O_2 in DMSO

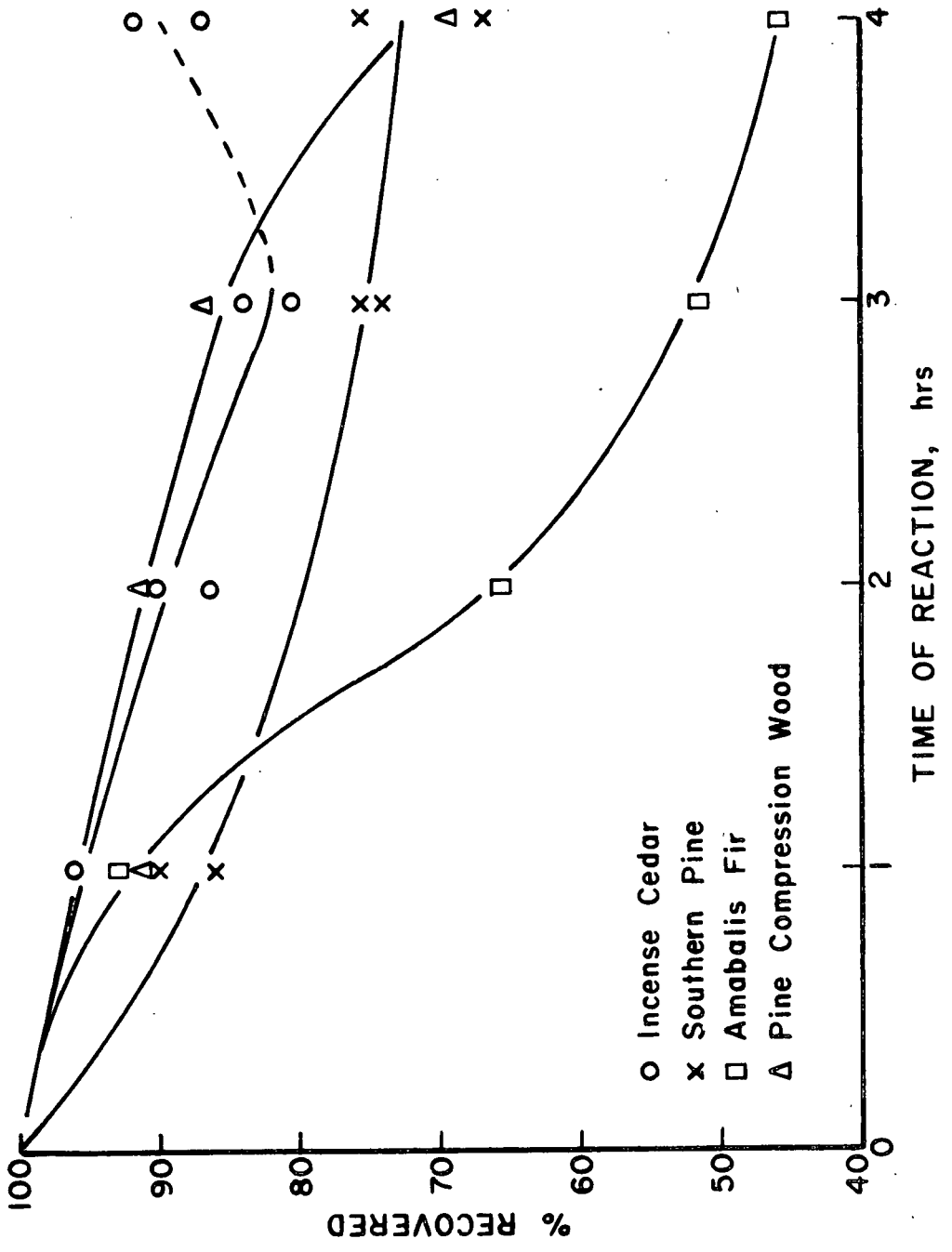


Figure 5. The Loss of Yield of Holocelluloses When Reacted With KO_2 in DMSO at Ambient Temperatures

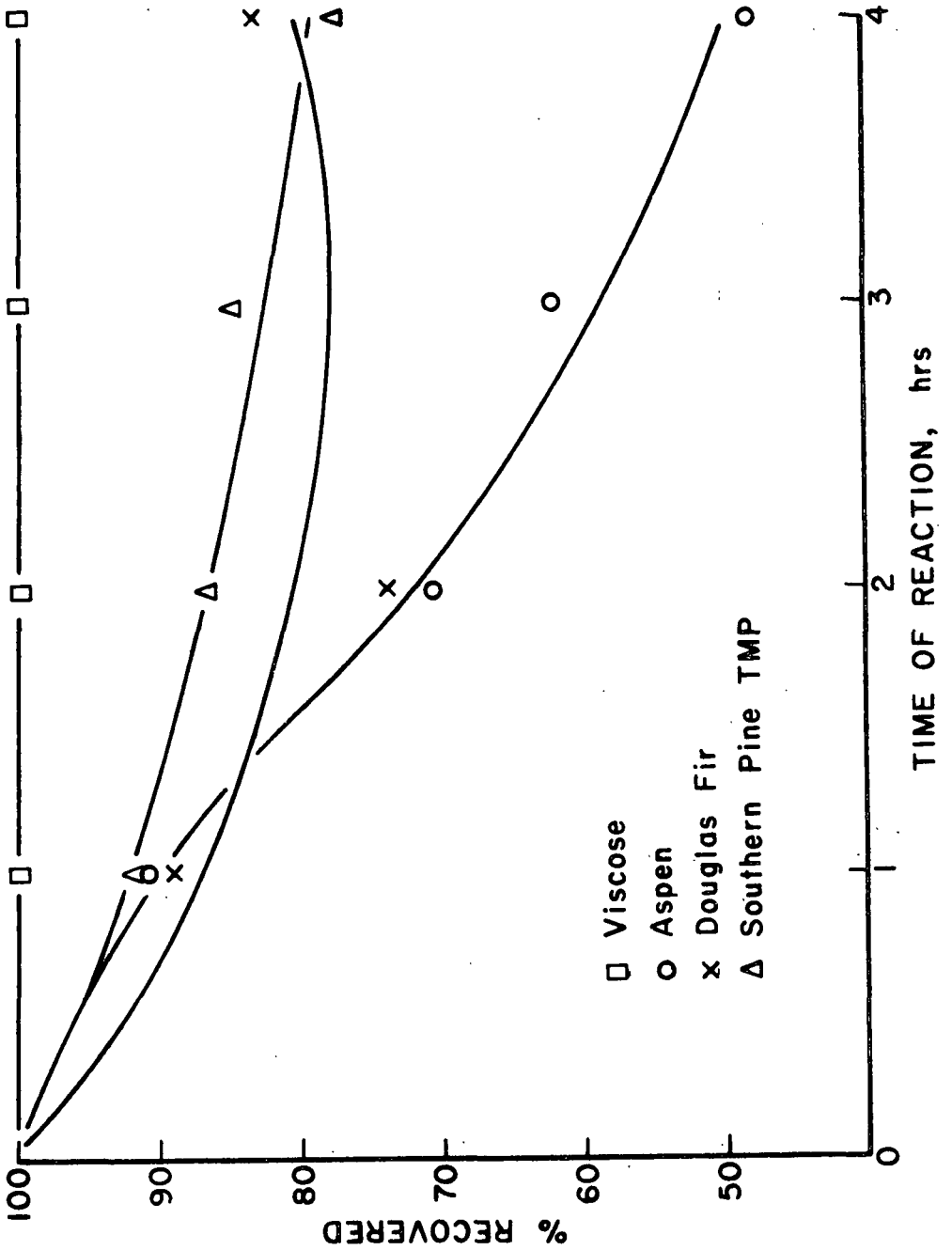


Figure 6. The Loss of Yield Fibrous Products When Reacted With KO_2 in DMSO at Ambient Temperatures

TABLE I

THE CHANGE IN CARBOHYDRATE CONTENT OF PULPS WITH TIME OF REACTION WITH KO_2

	Time of Reaction, hours	Polysaccharide Content, % of Original Pulp				Yield, %	Cuene Viscosity[a], cp
		Glucan	Galacto-glucomannan	Arabino-xylan	Total Lignin		
Southern Pine TMP	0	63.5	26.1	10.4	27.5	--	
	1	64.2	25.8	10.0	26.9	92	
	2	65.2	25.5	9.4	26.9	87	
	3	66.4	24.9	8.7	27.1	80	
	4	67.1	24.6	8.4	26.8	77	
Southern Pine Kraft 19 kappa	0	82.7	9.7	7.7	2.8	--	7.90
	1	83.5	9.9	6.4	1.5	98	2.56
	2	86.2	8.1	5.6	2.0	93	1.88
	3	88.9	6.8	4.3	1.6	93	1.70
	4	83.5	10.0	0.4	2.4	91	1.84
Southern Pine Kraft 35 kappa	0	81.8	10.0	7.2	4.5	--	37.0
	1	85.0	10.0	5.8	4.3	86	2.14
	2	87.4	8.1	4.5	3.4	81	1.72
	3	93.8	4.3	1.8	1.1	57	1.60
	4	96.4	3.3	0.7	1.6	50	1.59
Southern Pine Kraft 95 kappa	0	81.1	11.0	7.7	13.1	--	
	1	84.7	9.8	5.4	12.6	97	
	2	85.1	10.2	4.7	10.6	93	
	3	87.1	8.9	4.0	9.6	86	
	4	89.2	7.8	2.9	8.7	79	
Amabalis Fir Holocellulose	0	77.0	20.7	1.6	trace	--	
	1	82.4	16.6	1.2	--	86	
	2	91.0	7.4	0.6	--	81	
	3	94.1	5.1	0.7	--	57	
	4	96.2	3.2	0.6	--	50	

[a] 0.5% Cuene solution; Tappi T230.

show that KO_2 does not preferentially remove lignin but attacks carbohydrate with equal ease. The arabinoxylan type polysaccharides were the most susceptible to removal while the close parallel between galactoglucomannan and lignin reminds one of the possible existence of a lignin-carbohydrate bond (34). The preferential loss of hemicellulose is also characteristic of the reaction of holocellulose as well (Fig. 5 and 6). The loss of yield of southern pine TMP appeared to be due to the proportionate loss of both lignin and polysaccharide (Fig. 6). This behavior is in marked contrast to the response of the pulp to ozone observed by Lyse (33).

TABLE II

POLYSACCHARIDE CONTENT OF WATER-SOLUBLE EXTRACTS AFTER KO_2 OXIDATION

	Time of Reaction, hr	Polysaccharide Content, % of Extract			
		Glucan	Galacto-glucomannan	Arabino-xylan	Accountability
Southern Pine TMP	2	23.2	21.0	16.9	61.2
	3	40.8	11.4	7.4	59.6
	4	30.3	15.6	12.5	59.4
Southern Pine Kraft 95 kappa	2	17.7	25.2	18.5	61.4
	3	9.8	20.8	17.6	48.2
	4	19.8	22.6	18.5	57.9
Amabalis Fir Holocellulose	1	7.5	57.5	6.9	71.9
	2	23.5	36.3	4.1	63.9
	3	31.8	27.2	3.0	65.0
	4	38.6	19.6	2.1	60.0

The results obtained so far indicate that superoxide is not a selective delignifying agent, and qualitative examination of the brightness of reacted kraft pulps suggests it is not an effective bleaching agent as well. The response of the TMP to superoxide suggests many of the parameters governing the reaction with pulp fibers are not known. The role played by KO_2 is equally uncertain, and it is not known whether superoxide is the reactive species involved. The occurrence

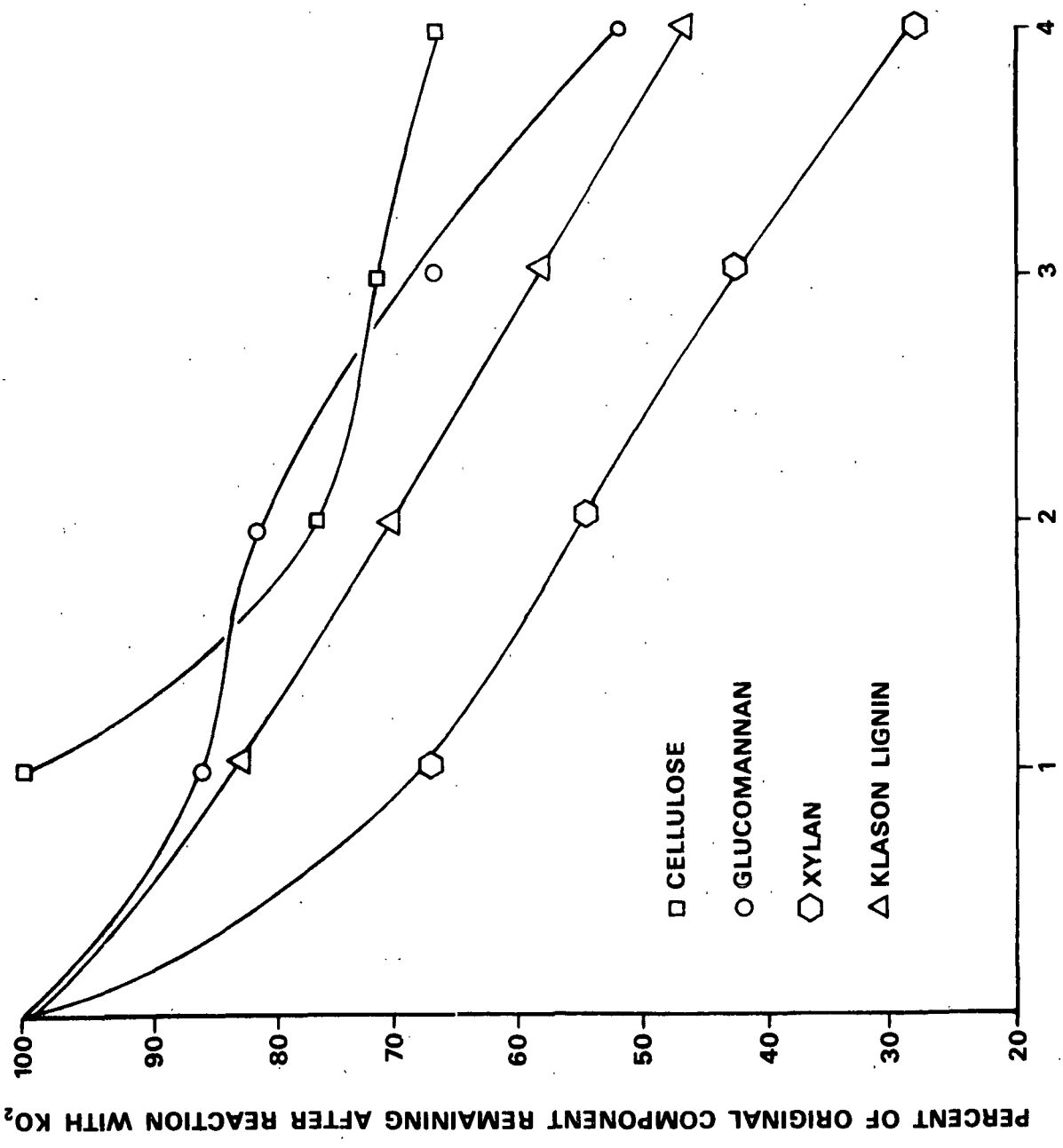


Figure 7. The Loss of Yield of Polysaccharide and Lignin Components from a Southern Pine Kraft Pulp (95 kappa) When Reacted With KO_2 in DMSO at Ambient Temperatures

of a rapid and preferential reaction of hydroxyl radical with DMSO to produce methane sulfonic acid and methyl radical (35) makes it unlikely that the hydroxyl radical participates in these reactions although it may contribute to degradation

$$\cdot OH + Me_2SO \rightarrow \cdot CH_3 + CH_3SO_2H \qquad (17)$$

during oxygen bleaching. Although the methyl radical is a powerful species and might contribute in some manner to the observed degradations, it would probably react preferentially with superoxide or oxygen. The presence of some intermediate species derived from oxygen (such as singlet oxygen or hydroxyl radical) can be detected under suitable circumstances which will be described later in this report. Kraft pulp does not react with Na_2O_2 in DMSO solution (Fig. 6). Thus the reaction of pulp does not occur as a result of the degradation of KO_2 in DMSO to peroxidic intermediates as has been suggested for other reactions in the literature (3).

The scanning electron microscope is a valuable tool for studying the changes in fiber shape and surface as a result of various kinds of manipulations. Most earlier photomicrographs suffer from distortions caused by surface tension forces which result during the drying process. This difficulty has been minimized by the use of critical point drying — a process in which the specimen is dried from carbon dioxide at the critical pressure and temperature of carbon dioxide. Since there is no liquid phase under those conditions, surface tension effects are minimized (36) provided all other solvents have been removed.

SEM micrographs of the pulps reacted with KO_2 indicate the loss of yield can be qualitatively correlated to the gradual exposure of the microfibrillar texture of the outer walls of the specimen. Figure 8 (3000X) shows the typical surface of a tracheid of a 95-kappa southern pine kraft pulp before reaction with

KO_2. The microfibrillar features are obscured by a layer of lignin and hemicellulose. No fines are present although some filmy tissues are adhering to the surface of the tracheid.

Figure 8. Southern Pine Kraft Pulp, 95 Kappa, Not Reacted With KO_2, #3462, 3000X

After four hours reaction with KO_2 under standard conditions, the microfibrillar structure of the tracheid becomes apparent as lignin and hemicelluloses are removed as shown in Fig. 9 (see also Tables I and II and Fig. 6 for chemical changes). This feature is well known and is attributed in the literature to the removal of noncellulosic substances from between cellulosic microfibrils. Although the samples were subjected to a vigorous agitation, few fines are observed

clinging to the tracheid surface or in the surrounding medium [compare these photographs with those of Giertz (37)]. The surface does have innumerable small holes which could represent points of chemical attack or a natural phenomena caused by the distortion of microfibrils by small residual drying forces. [See review articles by Jayme and Hunger (38) and Emerton (39)].

Figure 9. Southern Pine Kraft Pulp, 95 Kappa, Reacted 4 Hours With KO_2, #3494, 6000X

Similar features can be observed in an examination of SEM micrographs taken by Ruhanen in a recent A-291 research project at the Institute (40). The photomicrograph in Fig. 10 taken from his report shows the typical surface of a tracheid of a 25-kappa kraft pulp composed of 8% hardwood and 92% softwood (about

60% pines, remainder fir and spruce) which had been bleached by a conventional CEH sequence. The underlying microfibrillar structure is becoming apparent, but the outstanding feature is the occurrence of innumerable small holes. A similar feature is observed when this kraft pulp is bleached by a conventional CEDED bleaching sequence (Fig. 11). When the pulp is bleached by an experimental acid wash, peroxide, peroxide sequence (APP) the surface is much more corroded (Fig. 12), while the surface of the pulp bleached by an APPDED sequence appears to be the most affected as shown in Fig. 13 (probably due to the removal of the encrustants by the DED sequence). These micrographs suggest that the features seen in Fig. 9 (especially the holes) may be due in part to the removal of hemicellulose and the distortion of the underlying microfibrillar structure by drying forces.

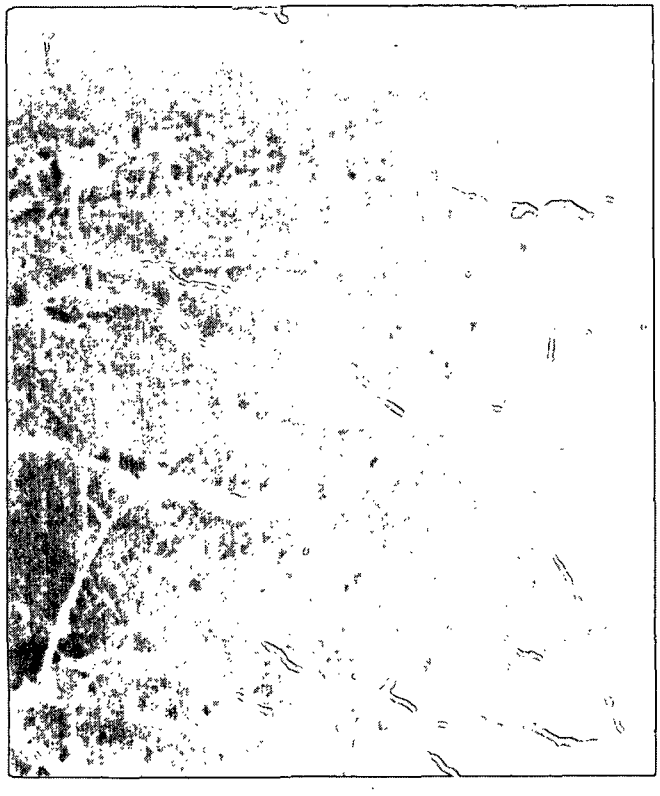


Figure 10. Northern Softwood Kraft Pulp, 25 Kappa, Bleached CEH, #5090 10,000X

Figure 11. Northern Softwood Kraft Pulp, 25 Kappa, Bleacked CEDED, #5091 10,000X

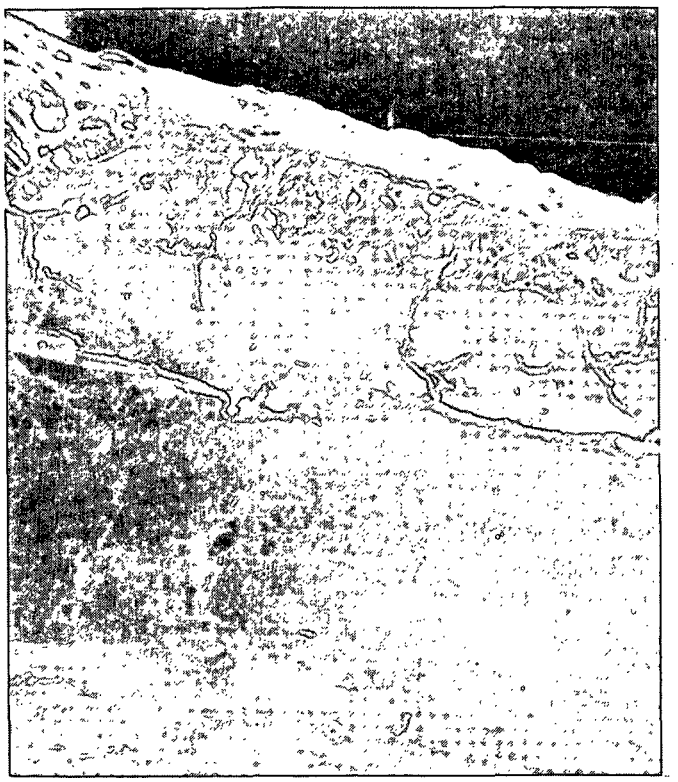


Figure 12. Northern Softwood Kraft Pulp, 25 Kappa, Bleached APP, #5088, 10,000X

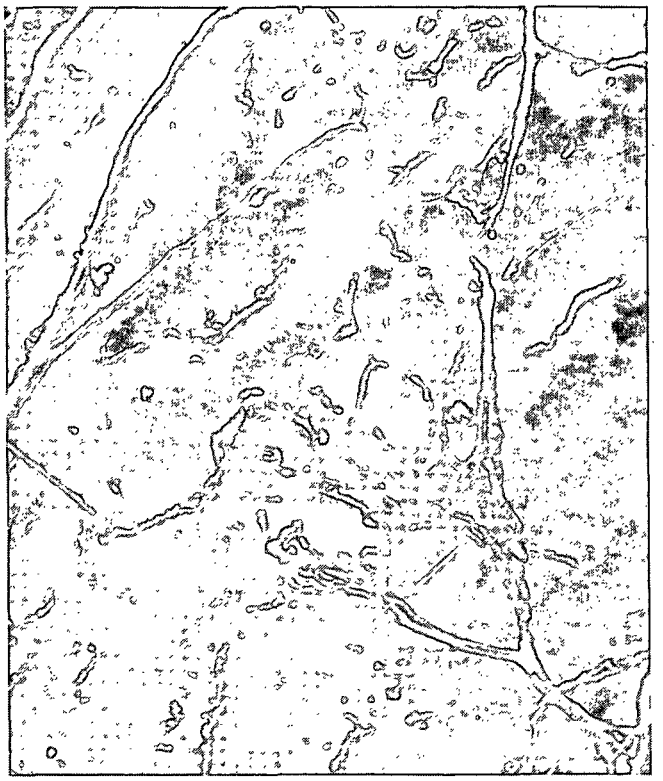


Figure 13. Northern Softwood Kraft Pulp, 25 Kappa, Bleached APPDED, #5089, 10,000X

Southern pine holocellulose tracheids behave in a similar manner to pine kraft pulp. Figure 14 illustrates the surface of a tracheid which has been gently fiberized with the assistance of dilute NaOH. Easily soluble polysaccharides such as arabinogalactans, certain xylans and galactoglucomannans and especially the pectic substances associated with the middle lamella have been removed (41). As a result, the underlying microfibrillar structure of the outer walls can be seen, and holes in this network are readily apparent (42). These holes probably result from the removal of hemicellulose and lignin since we believe the drying stresses to be minimal. A variation in the isolation of oxidized pulp

was employed in these experiments by eliminating the water wash and using methanol instead to remove residual oxidant and DMSO. The surface of the resulting tracheid shown in Fig. 15 is heavily encrusted with debris, fines, and microfibrillar aggregates. The underlying surface is microfibrillar in character and has many holes. If, now, water is used to destroy residual peroxide and to remove traces of DMSO, none of the surface contamination seen in the previous figure is visible. The water soluble components from the second (and most commonly employed) method of isolation can be recovered by alcohol precipitation, and the analyses of these fractions has been discussed earlier (see Fig. 7 and Table II). It is likely some of the debris seen in Fig. 15 are salts of alcohol-insoluble acids, and the rest may be highly oxidized polysaccharide components. The surface of the tracheid has obviously responded to the beating action of the standard shaking technique as a few fines typical of such action are also evident. At higher magnifications (>8000) much of the detail of the surface of this type material is lost and cannot be clarified by changing the focus of our present SEM equipment. This phenomenon results from distortions of the electronic image associated with localized heating and vibration of projecting surfaces.

After the sample is extracted with water, debris and fines on the surface of the pine tracheid are no longer evident in Fig. 16, although the fibrillar character of the walls remain. In this photomicrograph, minute distortions can be observed scattered about the surface of the tracheid. These resemble the distortions seen in Fig. 13 and are caused by tiny projections above the surface of the object being examined. The focus cannot be improved with the SEM equipment at the Institute. A more sophisticated instrument was made available to the Institute staff and an SEM photomicrograph (40,000X) of the distortions on the surface of a pine holocelluose tracheid oxidized for 4

Figure 14. Southern Pine Holocellulose, Not Reacted With KO_2, #3725, 4,000X

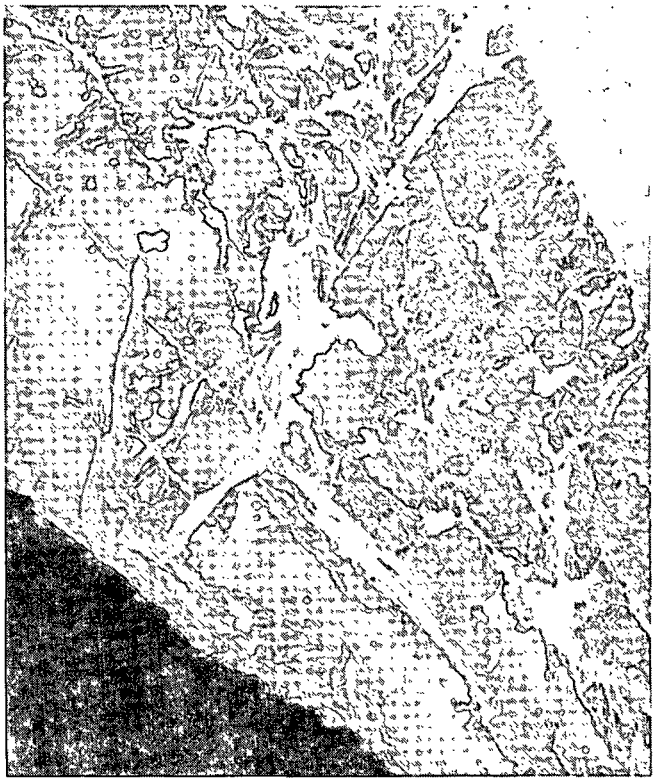


Figure 15. Southern Pine Holocellulose, Reacted 3 Hours With KO_2, Not Extracted with Water, #3752, 6,000X

hours with KO_2 is seen in Fig. 17. The surface of this tracheid is relatively smooth at this magnification except where holes have been burned into the surface. If the holes represent the space previously occupied by extracted material, the shape of the surrounding fibrils should be evident as can be seen around the holes in Fig. 14 and described by Jayme (38). The small holes in the surface of the oxidized pine tracheid are surrounded by small projections which may be broken fibrils. This could represent the degradative action of KO_2 on microfibrils of the outer wall. Only further research will show whether this is a common feature of superoxide and peroxide degradation of pulp (shown in the several micrographs).

It is tempting to speculate that the holes in the surface of extracted and/or conventionally bleached pulps will not exhibit this feature but will resemble the holes described by Jayme and others. It might be anticipated that those bleaching degradations caused by radical mechanisms speculated upon in the literature may show similar broken fibrils.

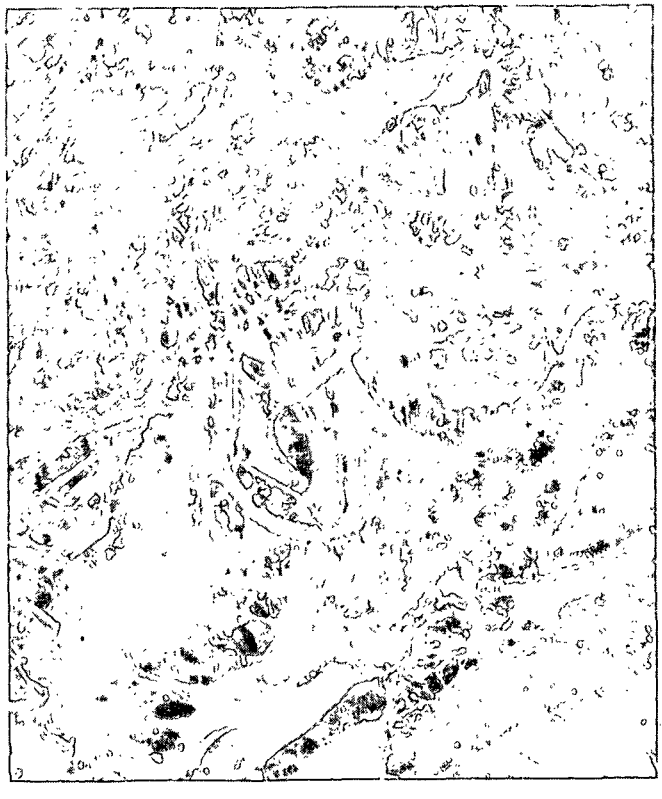


Figure 16. Southern Pine Holocellulose, Reacted 3 Hours with KO_2, Extracted with Water, #3759, 6,000X

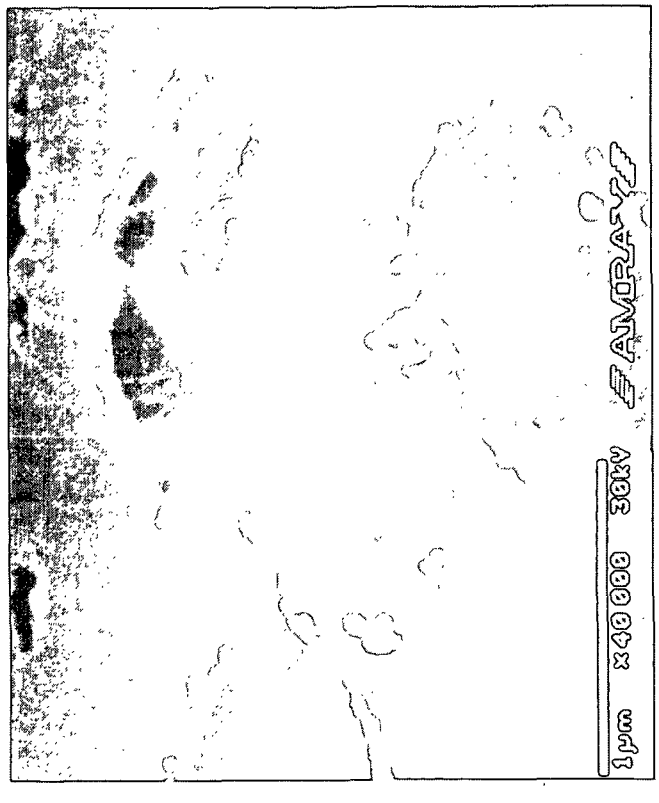


Figure 17. Southern Pine Holocellulose, Reacted 4 Hours with KO_2 Special Micrograph, 40,000X

The surface of cotton staple was also examined by SEM before and after reaction with KO_2. The surface of the purified DMSO-extracted staple cotton fiber before reaction with KO_2 is shown in Fig. 18. The microfibrillar texture of the secondary wall can be seen through the thin overlying outer wall layers. The collapse of the lumen is also apparent. It will be shown later that the loss of yield of cotton during reaction with KO_2 shows a significant induction period. The cotton surface shown in Fig. 19 records the damage after 5 hours reaction when the yield loss became significant. Some wall debris is still associated with the fiber. The most outstanding feature is the highly pitted and corroded nature of the wall layers. The degradation has penetrated the outer layers and has penetrated deeply into the secondary wall. Figure 20 (10,000X) gives a more highly magnified view of similar degradations. It is interesting to note that here too minute distortions of the electronic image are present and suggest the presence of innumerable broken microfibrils. Figure 21 shows that the degradative erosion can lead ultimately to the separation of fibrillar aggregates of the secondary wall. This behavior is similar to that exhibited by tracheids — especially compression wood tracheids — and may reflect the effect of mechanical action on the weakened secondary wall.

The reaction of viscose staple with superoxide was also briefly examined and little yield loss occurred after 4 hours of reaction. Figure 22 illustrates the surfaces of the unreacted control while Fig. 23, 24 and 25 show typical surfaces after 4 hours reaction with KO_2. Large sections of fibers do not appear to have reacted (Fig. 23), while examples of skin loss and highly localized erosion sites are evident in Fig. 24 and 25. The latter features, like the evidence in Fig. 17, suggest that the degradation starts at a point source on the wall and then proceeds in all directions until it is inexplicably stopped.

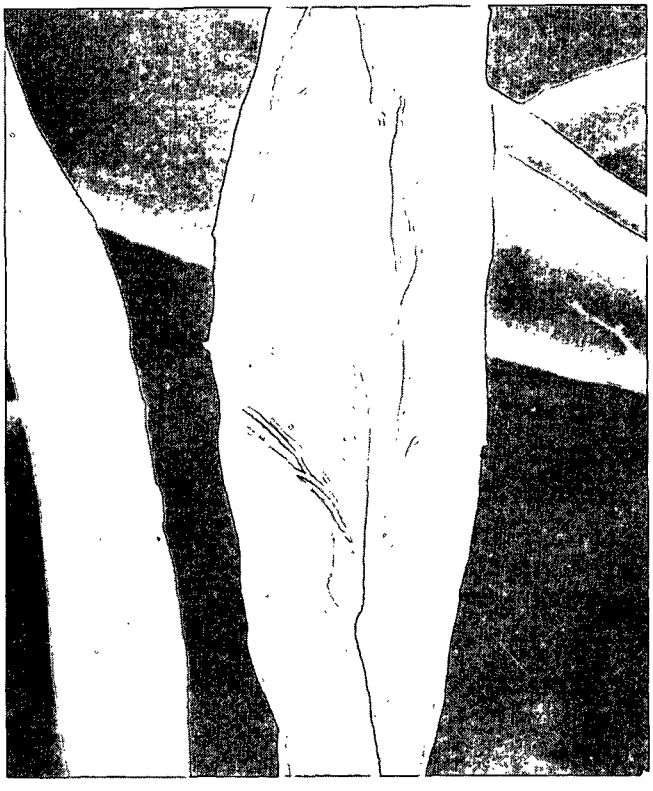


Figure 18. Cotton Staple, Not Reacted with KO_2, #4076, 2,000X

Figure 19. Cotton Staples, Reacted 5 Hours with KO_2, #5017, 3,000X

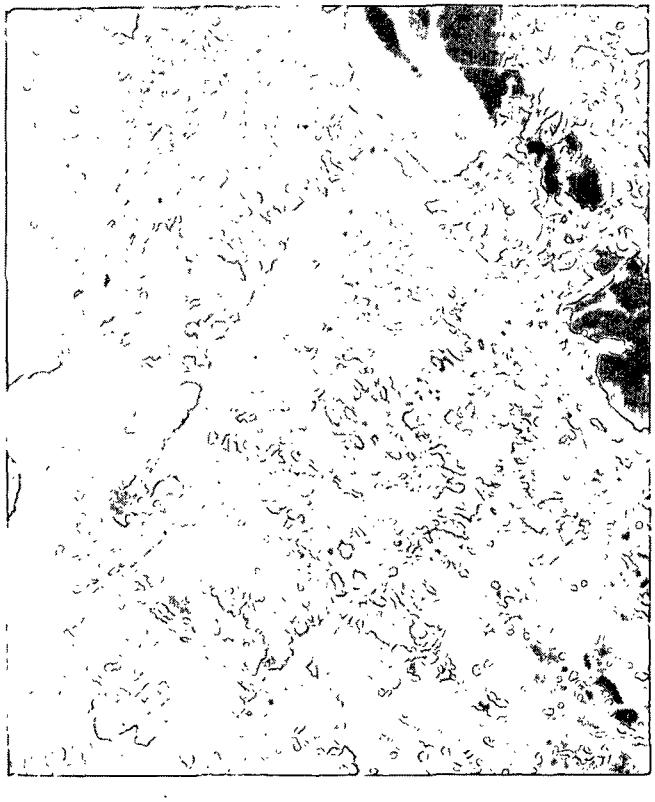


Figure 20. Cotton Staple, Reacted 5 Hours with KO_2, #5019, 10,000X

Figure 21. Cotton Staple, Reacted 5 Hours with KO_2, #5016, 3,000X

In the case of tracheids, the degradations are localized on a fiber, but where localized degradation appears, it appears in a random fashion. The degradations on viscose fibers can appear in a random fashion (as in Fig. 24) or along the longitudinal axis of the fiber as in Fig. 25. It is likely, therefore, that some unique feature can account for the initiation of this pitting degradation.

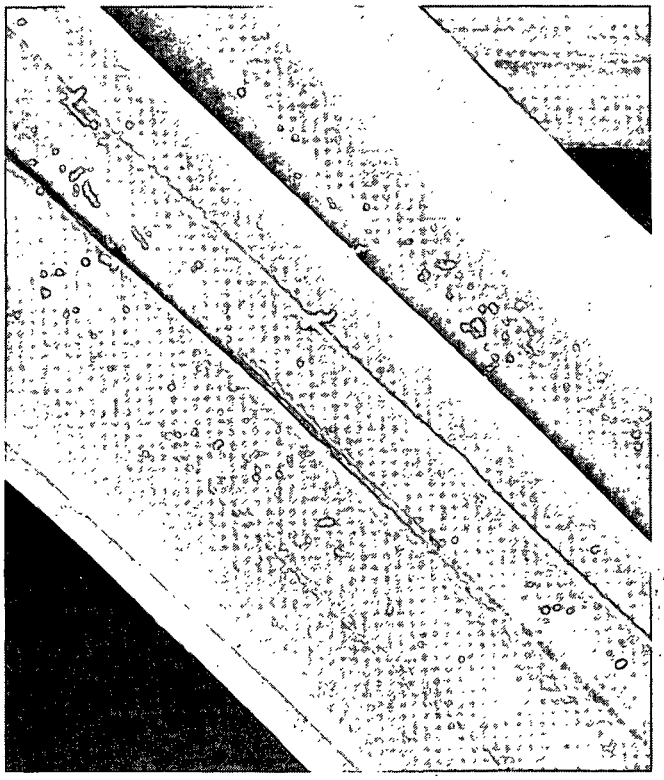


Figure 22. Viscose Staple, Not Reacted With KO_2, #3946, 5,000X

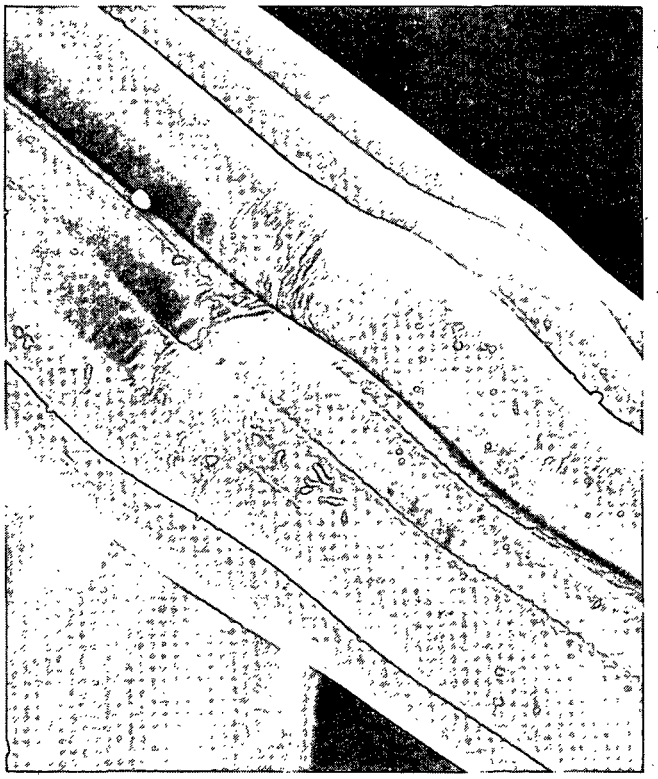


Figure 23. Viscose Staple, Reacted 4 Hours With KO_2, #3945, 5,000X

The relationship of mechanical agitation to yield loss was also investigated by several series of experiments. In one series, southern pine holocellulose was reacted with KO_2 at two different shaking rates — 232 and 180 shakes per minute. The plots in Fig. 26 demonstrate the dependence of yield loss on

shaking rate. In another experiment, samples of the same southern pine holocellulose were extracted with 18% NaOH containing 5% H_3BO_3 to remove as much hemicellulose as possible. After appropriate solvent exchange, the pulps were reacted with KO_2 at 232 and 180 shakes per minute. The plots in Fig. 26 demonstrate the dependence of yield on shaking rate. The prior removal of hemicellulose has no great effect on yield at the greater shaking rate, but does have questionable effect on yield of both extracted and unextracted pulps at the lower shaking rate. The comparison of behavior of the extracted and nonextracted pulps to KO_2 at different shaking rates is seemingly ambiguous because hemicellulose loss constitutes a large proportion of the loss of the unextracted pulp but not of the extracted pulp. The behavior at the different shaking rates of the rates of the two samples is likely dependent upon the surface available for reaction and not in the chemical nature of that surface.

Figure 24. Viscose Staple, Reacted 4 Hours with KO_2, #3967, 5,000X

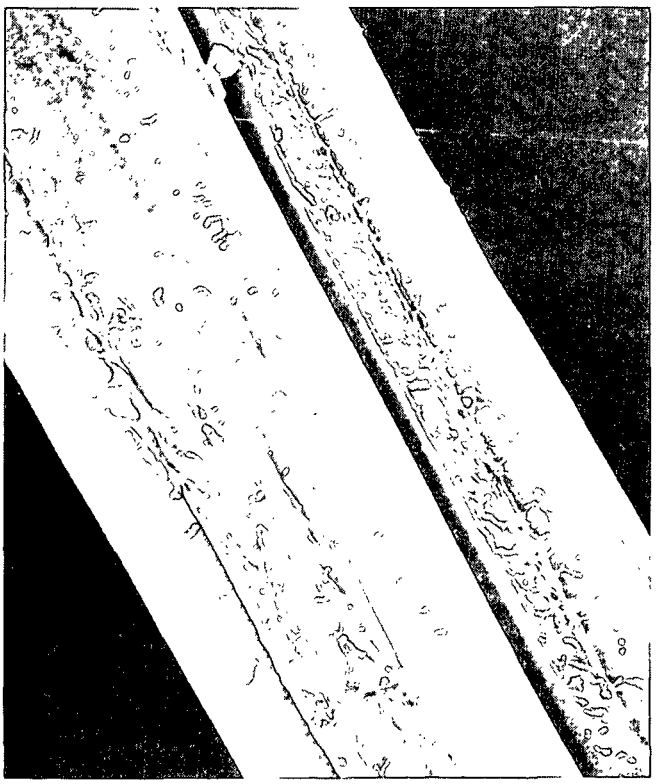


Figure 25. Viscose Staple, Reacted 4 Hours with KO_2, #3972, 4,000X

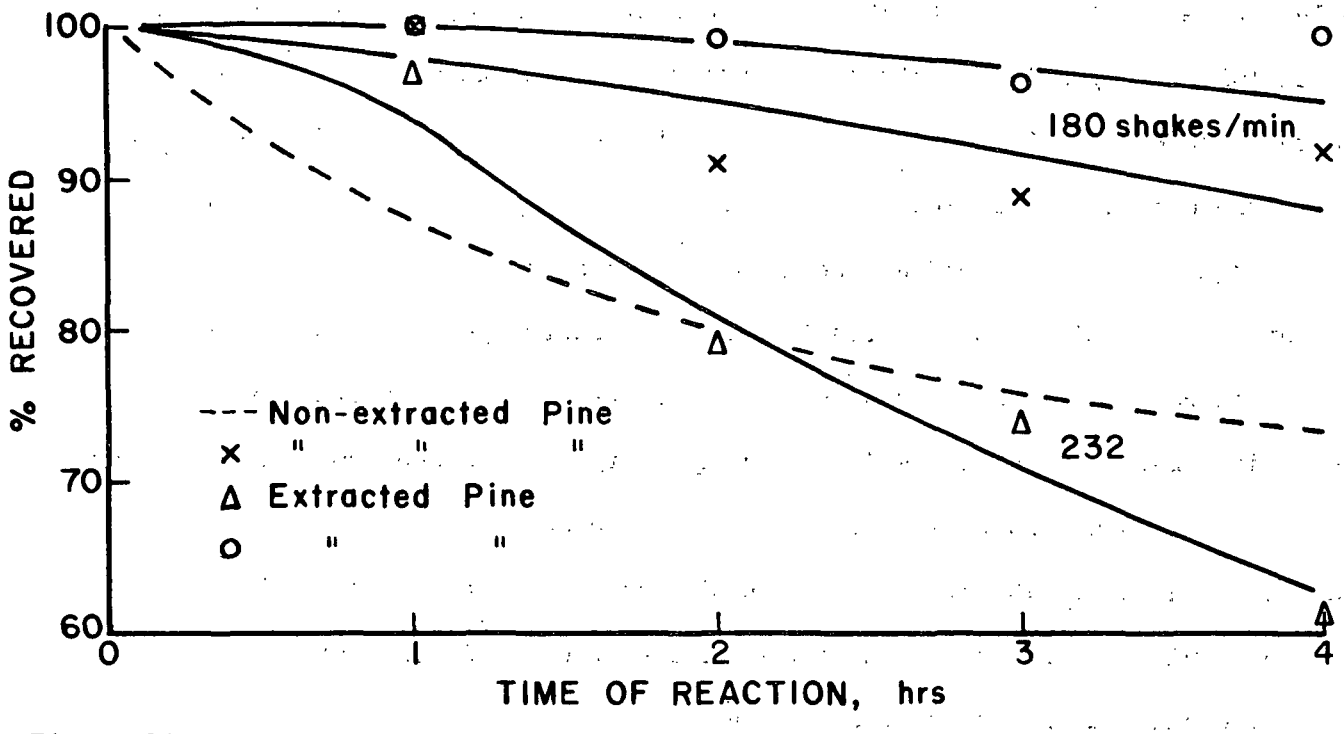


Figure 26. The Loss of Yield of Extracted and Nonextracted Southern Pine Holocellulose When Reacted at Different Shaking Rates in the Presence of KO_2 in DMSO at Ambient Temperatures

In another experiment, a laboratory-prepared 16-kappa spruce kraft pulp was reacted with KO_2 using different mixing devices. In one set, the reaction bottles were attached at the center and just within the circumference of an 8-inch disc which was 30° off vertical and rotated at 36 rpm as shown in Fig. 27. Another reaction was carried out by the standard reaction procedure described in Fig. 1. Two sets of oxidations were carried out — one using DMSO as wetting medium and the other using pyridine to confirm qualitative results which had indicated little difference between the two solvents as far as KO_2 reactions were concerned. The reaction in pyridine was slower because of the limited solubility of KO_2 in pyridine, however.

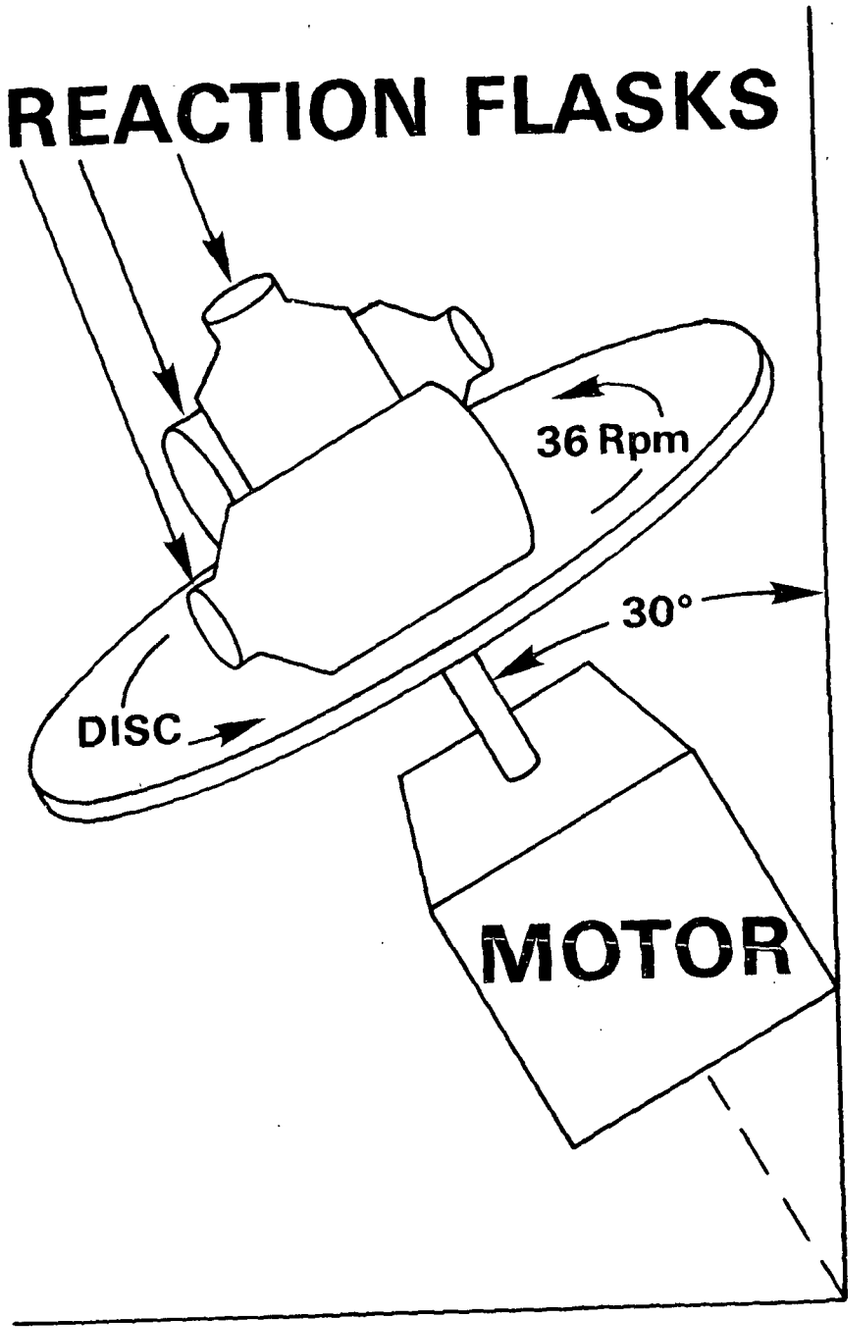


Figure 27. Schematic Diagram of Alternate Reaction System

The results (limited to a single 4 hour and 15 hour reaction time according to solvent) shown in Table III indicate that gentle rotation about the longitudinal axis of the glass reactor resulted in the least loss of yield while violent shaking by the standard reaction technique resulted in the greatest yield losses. Visual examination of the suspending solvents in all cases did not indicate any apparent difference in the yellow color of the dissolved KO_2, suggesting that the change in yield loss was not due to the less effective solution of KO_2 in the solvent. The better yield of the sample located on the circumference of the rotating disc compared to the control suggested mixing of KO_2 into the fibrous mass was not a contributing factor to the yield difference but that the violence of the mixing contributed to the loss of yield.

TABLE III

THE REACTION OF SPRUCE KRAFT PULP (16 KAPPA) WITH KO_2 IN DMSO OR PYRIDINE UNDER DIFFERENT MIXING CONDITIONS

	% Pulp Recovered After 4 Hours (DMSO) or 15 hr (Pyridine) Reaction with KO_2 at Room Temperature	
	DMSO Solvent	Pyridine Solvent
Rotated Axially	81.4	93.1
Related on Circumference of 8" Disc	74.3	88.4
Shaken by Standard Technique	49.7	53.3

In summary, many fibrous materials such as kraft, sulfite and holocellulose pulp of softwoods and hardwoods as well as cotton staple suffer large yield losses when reacted with KO_2 in aprotic solvents. The loss of yield is affected by lignin content, pulping process, and previous history of the sample as well as by mechanical action during reaction. The reaction behaves as if it proceeds through the accessible regions of the fibers as lignin and hemicelluloses

are removed before appreciable losses of cellulose occur. Since the yield losses of a tracheid are about the same even if the hemicellulose has been removed, it is concluded that any available polysaccharide surface will react if accessible to KO_2.

DMSO and pyridine behave similarly as reaction media. The loss of yield can be qualitatively followed by the appearance of fibrils on the outer surface of the tracheids. Although holes between fibrils occur during the reaction, some of the holes are thought to differ from those encountered after extractive reactions because they appear to be surrounded by broken fibrils. Examination of the surfaces of degraded cotton staple confirm the destruction of fibrillar components of the wall layer.

CLEAVAGE REACTIONS

The cleavage of tracheids and fibers into short fragments as a result of the action of KO_2 is the most unusual aspect of the response of fibers. This behavior can be easily recognized by visually comparing the fiber lengths shown in Fig. 28 and Fig. 29 (100X). The former micrograph shows the type of fiber types encountered in a 35-kappa southern pine kraft pulp. The latter micrograph illustrates what happens to that mixture when the pulp is reacted with KO_2 for 4 hours at room temperature and standard shaking. At somewhat higher magnification (Fig. 30, 300X), it can be seen that the cleavages are relatively clean and occur at approximately right angles to the fiber axis. Stress points (thought to be regions where additional cleavage is likely to occur) can also be noted in the figure. This type of degradation occurs with all the kraft, sulfite, holocelluloses, hardwood and softwood pulps, synthetic fibers such as rayon and nylon as well as cotton staple. It does not occur to any visual extent when southern pine TMP and

cotton wool are reacted, but a modified form of cleavage occurs when pine compression wood tracheids are reacted with KO_2.

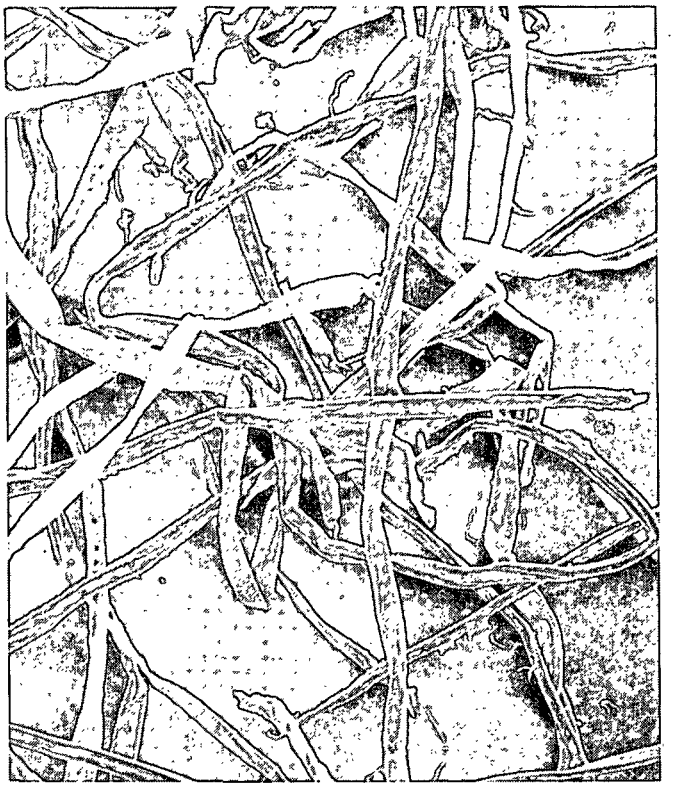


Figure 28. Southern Pine Kraft Pulp, 35 Kappa, Not Reacted with KO_2, #3426, 100X

Figure 29. Southern Pine Kraft Pulp, 35 Kappa, Reacted 4 Hours with KO_2, #3452, 100X

Views of the cleaved ends of tracheids are shown in Fig. 31 (4000X) and 32 (2000X). The breaks are clean and fibrillar aggregates within the wall structure can be seen. An SEM micrograph of the mechanically cut end of a cotton fiber is shown in Fig. 33 (3000X) for comparison. Since the beating action caused by the standard shaking device does not include any cutting action, the cleavages represented in Fig. 31 and 32 must result from very specific but as yet poorly understood degradative actions.

Figure 30. Southern Pine Kraft Pulp, 35 Kappa, Reacted 2 Hours with KO_2, #3438, 300X

Figure 31. Southern Pine Kraft Pulp, Reacted 4 Hours with KO_2, #4066, 4000X

Figure 32. Southern Pine Kraft Pulp, Reacted 4 Hours with KO_2, #4061, 2000X

Figure 33. Cotton Staple, Cut End of Staple, Not Reacted with KO_2, #4078, 3000X

Table IV illustrates the change in the average fiber length of a variety of fiber types after reaction for different lengths of time with KO_2 in the standard shaking apparatus. The slight increase in fiber length after 1 hour exhibited by some may be due to the selective destruction and removal of small cell types which are not present at later oxidation stages or in other kraft pulps. The results are also complicated by the fact that many very small fragments are not counted at the 4-hour reaction interval. Viscose staple, which did not undergo significant yield loss even after a 4-hour reaction time, was broken into fragments just as effectively as tracheids. The degradation mechanisms responsible for yield loss and fiber cleavage are, therefore, independent of one another in this instance and probably in the case of tracheids as well. On the average, the data in Table IV suggest an induction period occurs before the onset of appreciable fiber cleavage.

TABLE IV

THE CHANGE IN LENGTH OF VARIOUS FIBERS DURING REACTION WITH KO_2 IN DMSO AT ROOM TEMPERATURE

Time of Reaction, hr	0	1	2	3	4
Spruce kraft (16 kappa)	1.2	1.5	0.8	0.8	0.7
Southern Pine Kraft 19 kappa	1.6	1.6	0.8	0.7	0.8
Southern Pine Kraft 35 kappa	1.3	0.7	0.8	0.6	0.6
Pine Compression Wood Holocellulose	1.1	1.1	1.1	0.9	0.8
Incense Cedar Holocellulose	1.3	1.2	0.9	0.7	0.7
Viscose Staple	3.3	3.2	1.7	1.1	0.7

The cleavages illustrated in Fig. 34 and 35 are typical of southern pine holocellulose tracheids and do not seem to differ greatly from those from pine kraft tracheids. Figures 36 and 37 show partially cleaved tracheids which are still held together by residual lamellae. It is possible a combination of chemical degradation and mechanical disruption is responsible for cleavage, but if disruption were a major factor, smooth cleavages would not be expected unless some structural characteristics of the tracheid were also contributing factors.

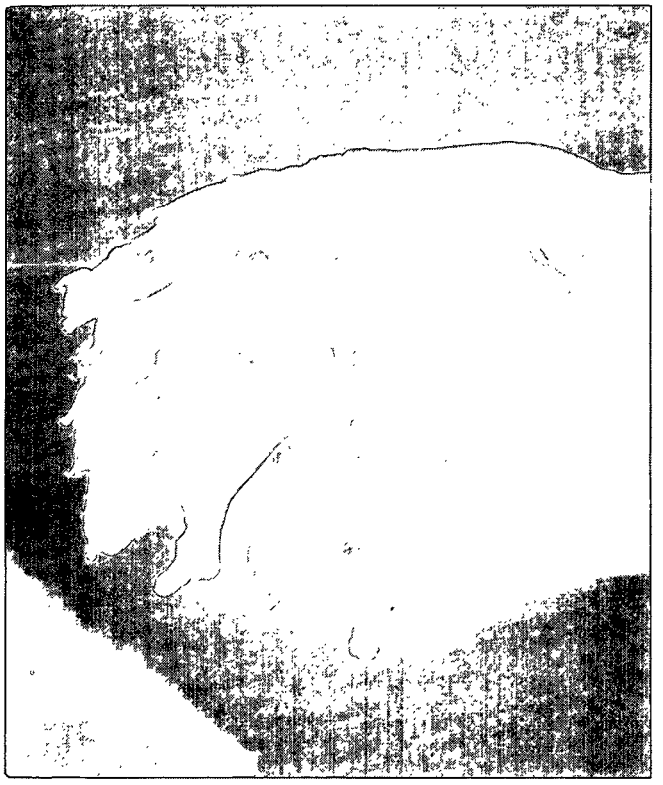


Figure 34. Southern Pine Holocellulose, Reacted 4 Hours with KO_2, #4054, 2000X

Figure 35. Southern Pine Holocelluose, Reacted 4 Hours with KO_2, #4056, 3000X

Figure 36. Southern Pine Holocellulose, Reacted 4 Hours with KO_2, #3757, 2000X

Figure 37. Southern Pine Holocellulose, Reacted 4 Hours with KO_2, #4052, 1500X

Slightly different degradative behavior is observed in the case of the tracheids from pine compression wood. Little degradation is evident after 1 hour of reaction (Fig. 38), but after 4 hours, the tracheids are smaller fragments (Fig. 39). The outer surface of the compression tracheids degrades in a different manner than the surface of a normal tracheid as can be seen from a comparison of Fig. 40 and 41. The surface of the normal pine tracheid is more resistant to degradation and does not have the worn and tattered appearance of the compression wood tracheid (Fig. 40).

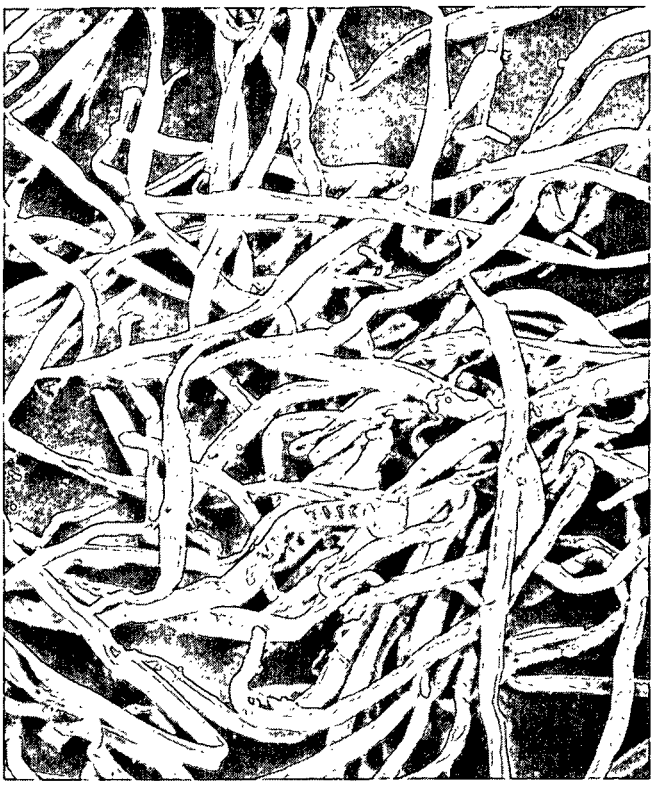


Figure 38. Pine Compression Wood Holocellulose, Reacted 1 Hour with KO_2, #3768, 100X

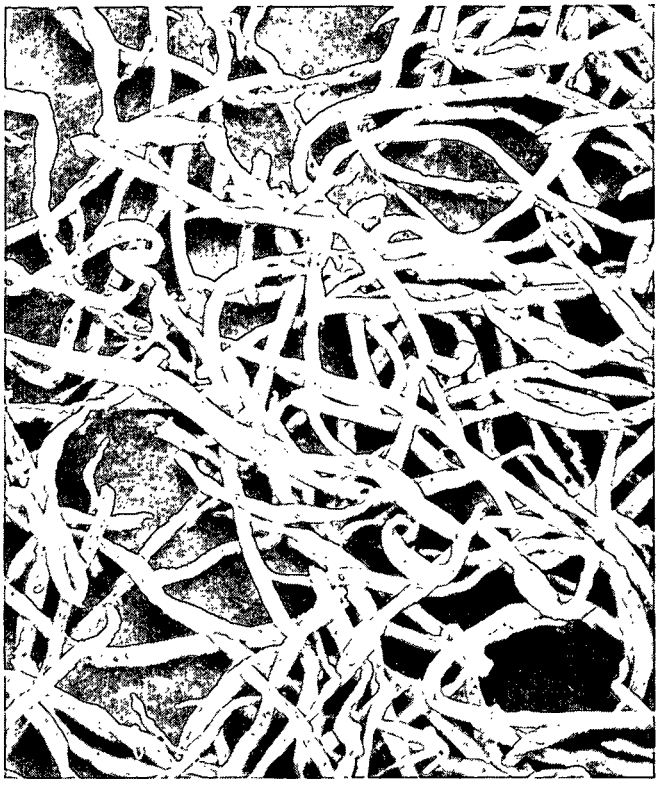


Figure 39. Pine Compression Wood Holocellulose, Reacted 4 Hours with KO_2, #3794, 100X

Figure 40. Pine Compression Wood Holocellulose, Reacted 4 Hours with KO_2, #3795, 300X

Figure 41. Pine Compression Wood Holocellulose, Reacted 4 Hours with KO_2, #3763, 300X

Examination of Fig. 42 and 43 illustrates one type of fiber cleavage that resembles the cleavages of normal pine tracheids (see Fig. 31, 32). Differences in the secondary wall architecture of the two tracheid types could account for the slight differences in detail. As mentioned above, the outer wall of the compression tracheids exhibits considerable degradation compared to normal walls. This is again evident in the previous two electron micrographs and in Fig. 44, 45 and 46. The loosening of the bonding of the outer wall to the secondary wall has allowed the fibrillar aggregates or lamellae of the secondary wall to separate with dramatic pictorial effects. A similar behavior of compression wood tracheids as a result of beating has been observed by Dadswell, Wardrop and Watson (43). Some of the lamellae are broken in Fig. 44, but the halves are held together by the remainder. There is less evidence for the cleavage of wall lamellae in Fig. 45 and in Fig. 46. The reason for this behavior of the outer wall of compression tracheids is not known but may result from physical deformities of that layer. Figure 47 shows the outer wall of compression wood in the process of degradation. The cleavage of the transverse fibrils (approximately perpendicular to their longitudinal axis) seems to follow a path of structural deformation pre-existing on the wall, and the existence of short fibrillar stubs is apparent at this magnification.

The existence of short fibrous residues averaging 0.6 mm after the reaction of pulp with KO_2 suggested another approach to understanding this unusual degradation. A southern pine holocellulose whose fiber character before reaction is shown in Fig. 48 was reacted with KO_2 to give fiber fragments shown in Fig. 49. The fiber length had been shortened to 0.8 mm. A small sample was dispersed in water and placed in an ultrasonic generator (used for the cleaning of GLC equipment) and subjected to ultrasonic energy for 30 minutes at room temperature. The results (Fig. 50) show that the lengths of the microfibrillar debris

Figure 42. Pine Compression Wood Holocellulose, Reacted 4 Hours with KO_2, #4046, 2000X

Figure 43. Pine Compression Wood Holocellulose, Reacted 4 Hours with KO_2, #4049, 3000X

Figure 44. Pine Compression Wood Holocellulose, Reacted 4 Hours with KO_2, #3796, 1000X

Figure 45. Pine Compression Wood Holocellulose, Reacted 4 Hours with KO_2, #3798, 1500X

Figure 46. Pine Compression Wood Holocellulose, Reacted 4 Hours with KO_2, #3800, 2000X

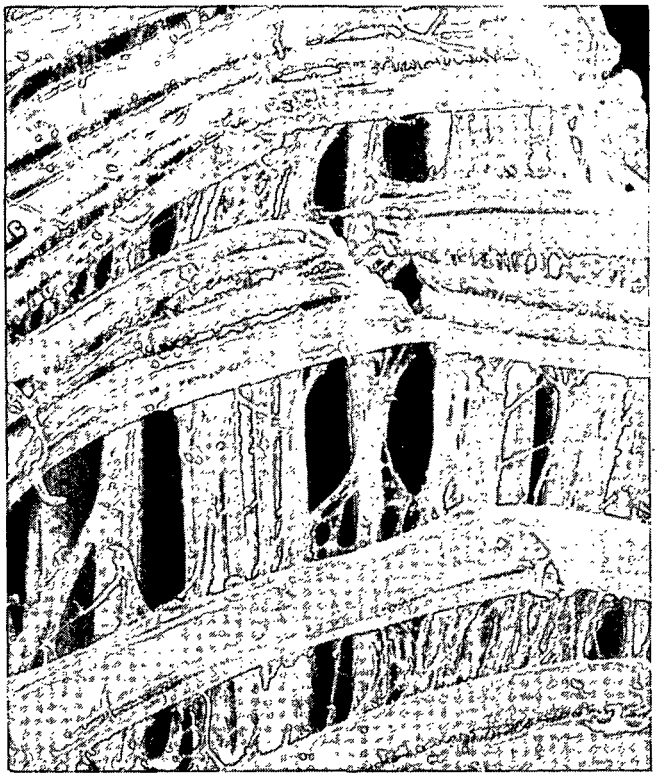


Figure 47. Pine Compression Wood Holocellulose, Reacted 3 Hours with KO_2, #3793, 6000X

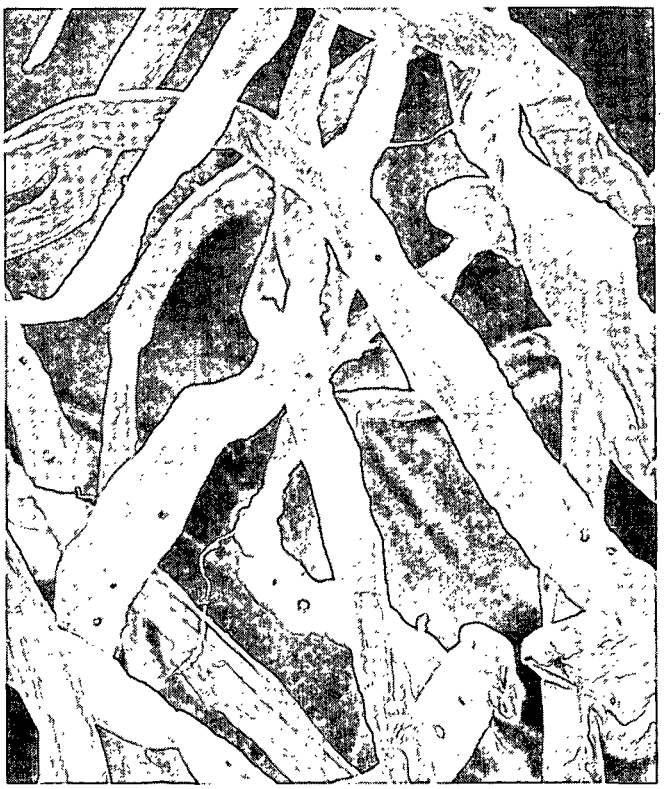


Figure 48. Southern Pine Holocellulose, Not Reacted with KO_2, #3720, 300X

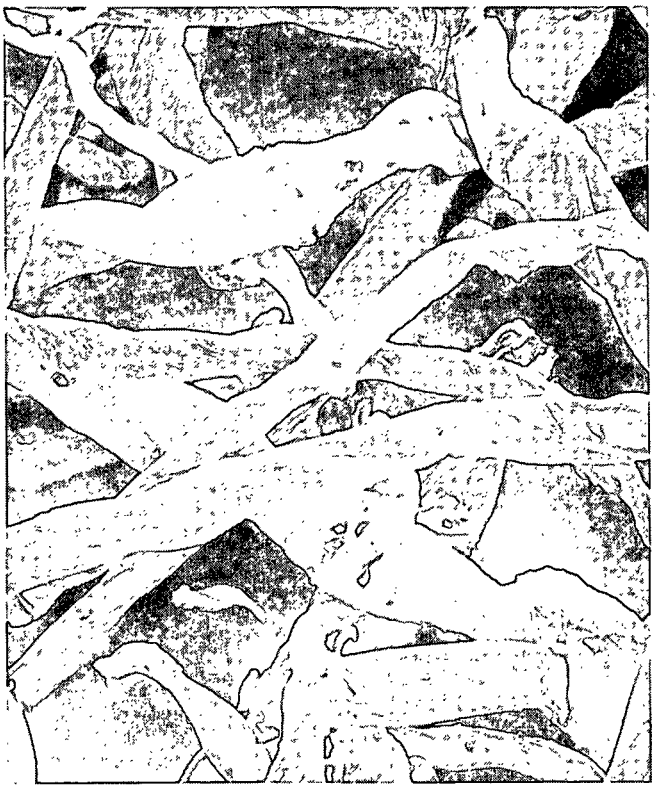


Figure 49. Southern Pine Holocellulose, Reacted 4 Hours with KO_2, #3762, 300X

are not equal to the length of the original degraded fiber fragment. Higher magnification (Fig. 51) shows that relatively thick nonfibrous particles exist in addition to the expected fibrillar debris. Higher magnification of these particles (Fig. 52 and 53) shows some of the details and the existence once again of very thin fibrillar stubs which adversely affect the resolution of the electron micrograph. These results indicate that the degradation of fibrils and hence of the cellulose is not restricted to the cleavage points so obvious in the previous electron micrographs but extends within the apparently undegraded portion of the fiber as well. As conjectured earlier, the cleavage of the tracheid may reflect the action of stresses and strains on these chemically weakened portions of the fiber. Consistent with this conjecture is the observation that single tracheids (if never dried) no longer exhibit elasticity after 1 hour of reaction with KO_2 but instead bend like a piece of string when pushed with a dissecting needle. The use of this or similar techniques before beating operations is intriguing.

Another experiment attempting to elucidate the effect of tracheid architecture on response to degradation by KO_2 was made when the action of that chemical was compared at 2 rates of shaking of southern pine holocellulose which had and had not been extracted with 18% NaOH + 5% H_3BO_3 to remove most hemicellulose components. In the previous section it was noted that extraction of hemicellulose before reaction had little influence on the yield of pulp recovered after reaction with KO_2 even though hemicellulose had been extracted. The rate of shaking did adversely affect the yield of pulp after reaction, however.

The effect of these treatments upon fiber length distribution is given in Table V. Even though extraction itself did cause reduction in the average fiber length (without reaction), the treatment caused an even greater loss of average fiber length when reacted at 232 shakes per minute. The slower shaking

Figure 50. Southern Pine Holocellulose, Reacted 4 Hours with KO_2, Ultrasonic Treatment, #4010, 300X

Figure 51. Southern Pine Holocellulose, Reacted 4 Hours with KO_2, Ultrasonic Treatment, #4011, 3000X

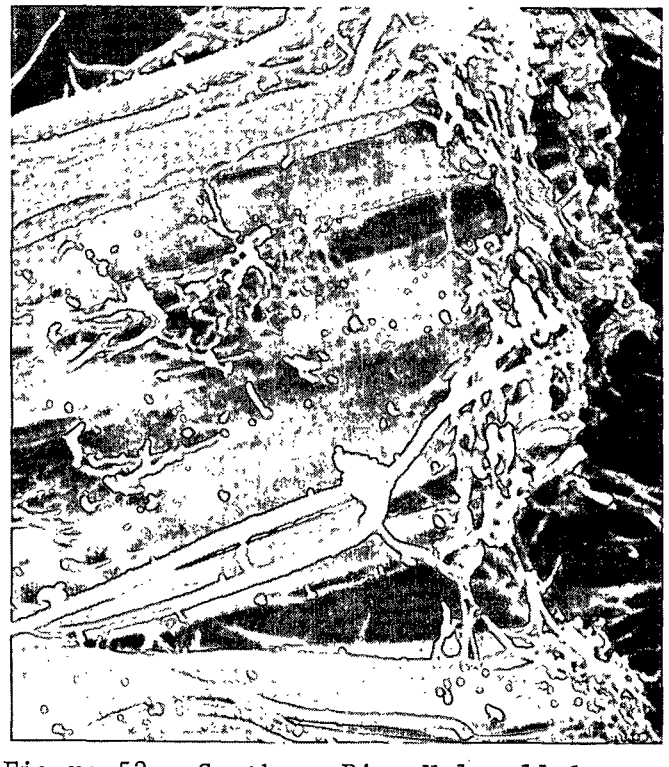


Figure 52. Southern Pine Holocellulose, Reacted 4 Hours with KO_2, Ultrasonic Treatment, #4011, 3000X

Figure 53. Southern Pine Holocellulose, Reacted 4 Hours with KO_2, Ultrasonic Treatment, #4015, 7000X

rate (180 shakes/minute) correlated with longer average fiber lengths, although the lengths of the two treatments at the lower shaking rate were about equal. The results suggest that changes in the molecular architecture of the cellulose as a result of alkaline treatment can cause changes in the degree of fiber degradation when subjected to vigorous mechanical action, but these differences disappear when the tracheids are subject to less vigorous action.

TABLE V

CHANGES IN THE FIBER LENGTH[a] (ARITHMETIC AVERAGE) OF SOUTHERN PINE HOLOCELLULOSE AS A RESULT OF HEMICELLULOSE REMOVAL AND OXIDATION WITH KO_2

	Time of Reaction, hr				
	0	1	2	3	4
Nonextracted (standard shake)	2.3	1.1	0.7	0.7	0.7
Nonextracted (slow shake)		2.1	1.6	1.0	1.0
Extracted (standard shake)	2.0	1.1	0.6	0.7	0.4
Extracted (slow shake)		1.3	1.7	0.9	0.9

[a] Fiber length in mm.

The degradation of cellulose by KO_2 was investigated using the high pressure liquid chromatography (HPLC) technique developed at The Institute under Project 3284. Cotton staple was chosen for this investigation because of the absence of lignin, the elimination of chloriting degradations if holocelluloses were to be used, and because the lack of hemicelluloses would simplify the interpretation of degree of polymerization (DP) distribution curves. Because of the novelty of the HPLC technique, the precautions and techniques necessary for the success of the investigation will be mentioned briefly.

The cotton samples after reaction with KO_2 were washed with methanol to eliminate residual oxidant and were then reduced with aqueous $NaBH_4$ to stabilize the degraded cellulose to subsequent alkaline treatments. After the removal of boron by acidification and washing with anhydrous methanol, the samples were isolated by freeze drying from water. These samples dissolved readily when reacted under prescribed conditions with phenyl isocyanate.

The unreacted control samples of cotton staple would not react with phenyl isocyanate to give soluble carbanilate esters. The controls were therefore dissolved in DMSO-paraformaldehyde to destroy their crystalline structures. The polymer was then precipitated as an amorphous derivative, freed of DMSO and formaldehyde, and isolated by freeze drying. These samples would give soluble carbanilate esters when reacted with phenyl isocyanate.

The molecular weight distributions of the carbanilate esters were determined by HPLC techniques developed by Schroeder (44). A plot of the uncorrected DP distribution curves against elution volume gives a symmetrical shape; a plot of weight average DP against oxidation time is given in Fig. 54. The results show that the cellulose is very rapidly degraded by KO_2 and the $DP_{(w)}$ is diminished to 1/9 of its original value after 1 hour at room temperature. See Appendix I for DP_n, DP_w, DP_{max} and DP viscosity values for cotton and its degradation products. The symmetrical shapes of the curves do not suggest that only the accessible parts of the fiber were attacked but that the degradation rapidly penetrated all portions of the fiber. This sensitivity to degradation can be explained if free radical degradations can proceed through the solid phase of the fiber. Such degradations would depend upon random radical initiation at the surface of a fibril within the fiber followed by free radical propagation until a termination reaction occurs. This radical mechanism could also occur in an aqueous medium, for, once initiated, the reaction would proceed rapidly into the accessible and probably crystalline regions of the cellulosic fibril and be free from water-induced termination reactions.

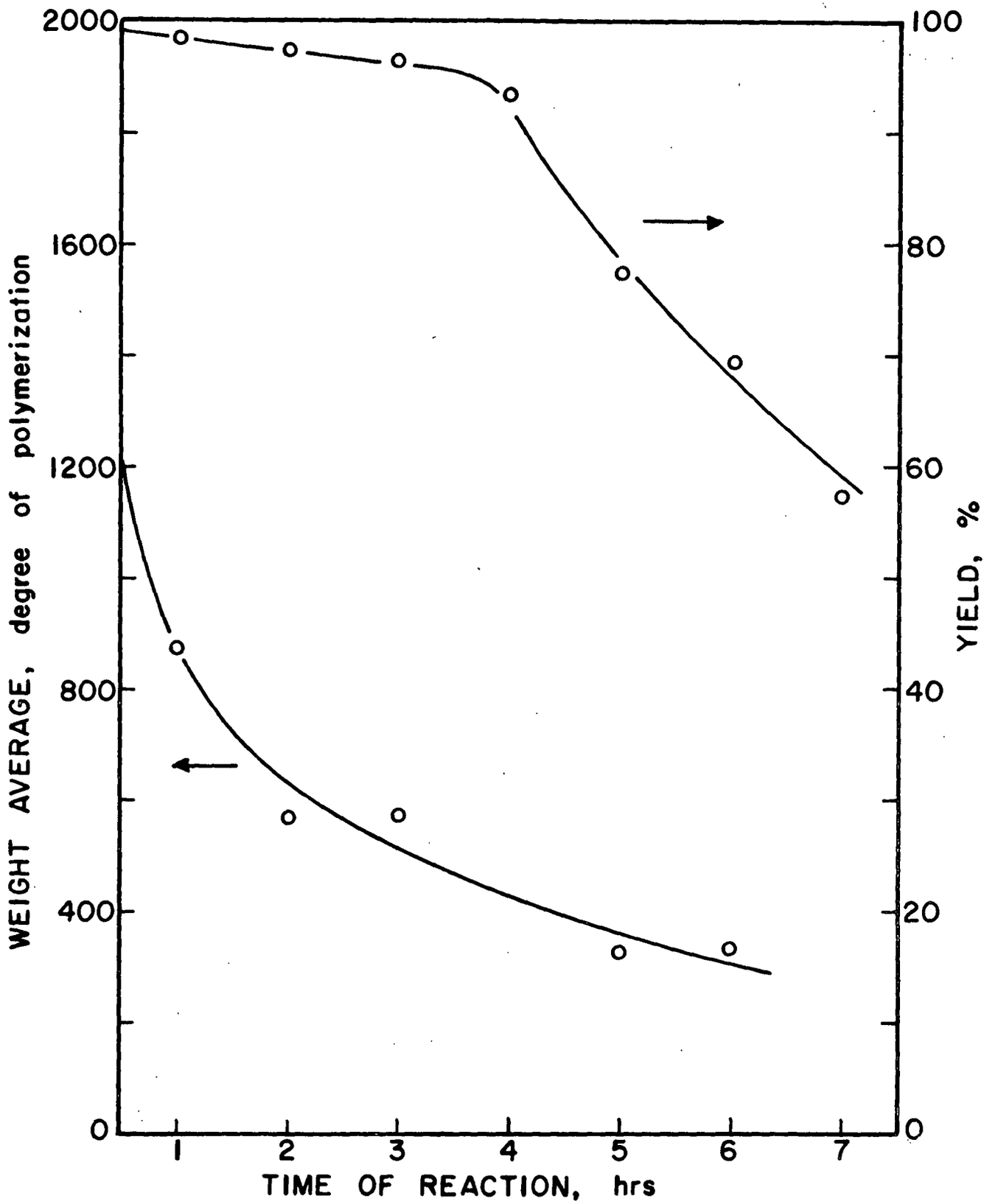


Figure 54. The Change in $DP_{(w)}$ and Yield of Cotton Staple Reacted with KO_2 for DMSO at Ambient Temperature

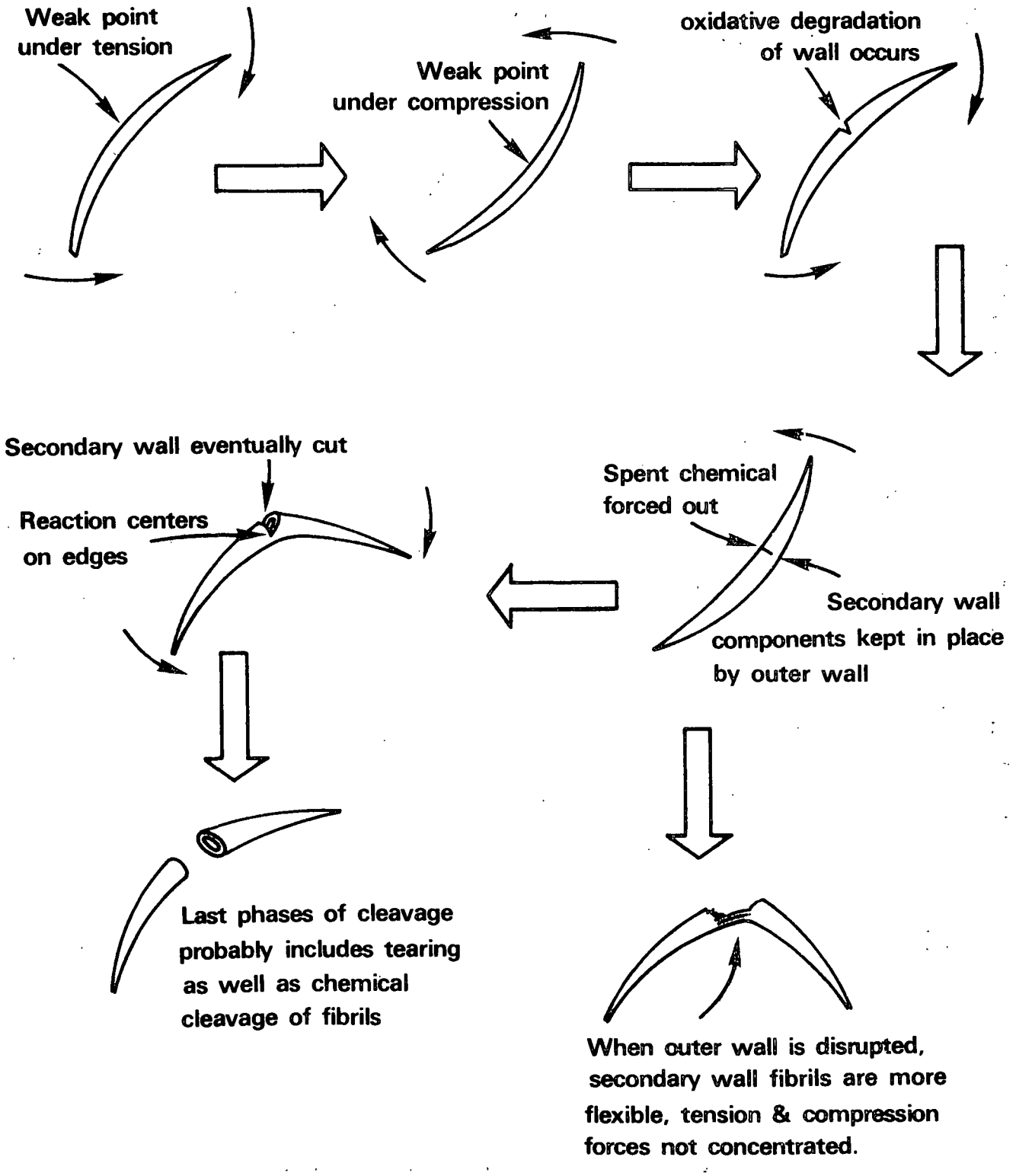


Figure 55. A Mechanism for the Cleavage of Tracheids and Fibers

DISCUSSION AND SUMMARY

The cleavage of tracheids and staple fibers into shorter fragments by KO_2 in aprotic solvents occurs rapidly, frequently after a short induction period. Exceptions exist in the case of pine TMP pulp, Avicel and cotton wool. The cleavage reaction is favored by mechanical treatment. The degradation seems to occur at about right angles to the fibrillar axis, and the broken ends do not have a shredded appearance typical of tearing. As suggested in earlier SEM photographs, the chemically cut ends do have a loose appearance, however, which contrasts with the compressed appearance of the cut ends of cotton staple. The wall layers and the contents of the secondary wall do not seem to be firmly bonded to one another as a result of the KO_2 treatment.

Compression wood tracheids are somewhat more resistant to cleavage. This behavior may be associated with the different fibril angle of the secondary wall and/or to the destruction of the outer wall layers. The latter effect would not hold the contents of the tracheid rigidly within the tracheid during flexing and hence minimizes stained locations as indicated in Fig. 55. The change in weight average degree of polymerization (DP_w) distribution of the cellulose of cotton staple was examined. The symmetrical shape of the distribution curves suggests localized degradation does not occur as would be anticipated if cellulose change occurred only at fiber-change points, while the rapid loss of DP_w in contrast to the slow initial yield loss with time of reaction (combined with empirical kinetic considerations) suggests that mechanisms paralleling acid hydrolysis do not occur.

Although the yield loss between extracted and nonextracted southern pine holocellulose reacted with KO_2 is not altered by that extraction, the extent of fiber cleavage is dependent upon such treatment and upon mechanical shaking.

This observation reinforces the hypothesis that, although the chemical mechanisms of degradation may be the same in both cases, yield loss depends upon accessibility, while cleavage depends on the effect of stresses on fiber structure.

As a result of the experiments performed to date, it is concluded that the cleavage of tracheids is initiated by a reaction between superoxide (in one of its forms) and a mechanically stressed portion of a fiber as indicated in Fig. 56. Penetration cannot be a major factor since viscose staple is cleaved with equal ease. The degradations would be continued at the weakest portion of the tracheid because that position would be susceptible to further stress. The chemical nature of the reaction is not known but may be free radical in character.

The size of the fibrils of the secondary wall of the short sections of tracheid was determined by shredding the outer wall by an ultrasonic treatment. The small size of the resulting debris and the lack of a long fibrillar character of the debris suggests that degradation has occurred throughout the whole wall and not only at localized positions where cleavage ultimately occurs. This behavior can be imagined to occur at those points where the wall is least crystalline as illustrated in Fig. 56) since the stresses caused by bending would be concentrated there and not at the stronger crystalline regions.

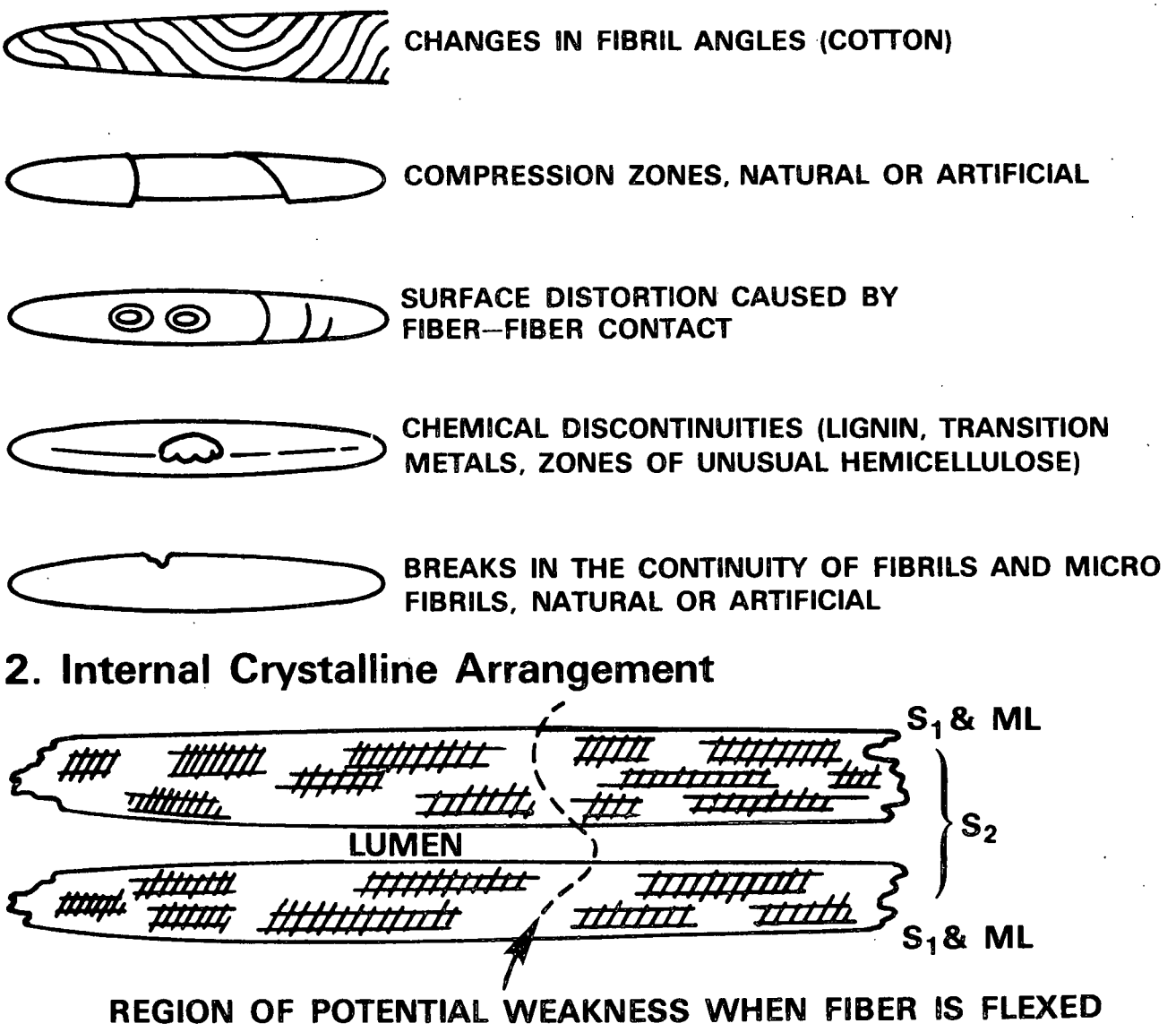


Figure 56. Source of Weak Points on Fiber Wall

REACTIONS IN AQUEOUS AUTOXIDATIVE SYSTEMS

INTRODUCTION

The degradation of pulp with KO_2 in DMSO or pyridine does not represent an adequate model for the study of the effect of radicals generated by commercial oxygen and peroxide bleaching systems on cellulose. It does give an idea of the complexities to be anticipated during the more ideal studies. Several other reaction systems to study these effects are either under way at the present time or are being planned for completion in the near future. Amongst these are reactions to study the effect of superoxide on pulp under aqueous conditions. Because of the short lifetime of superoxide in water and because of the difficulty of ensuring good mixing with pulp in the short period of time necessary, direct additions of KO_2 to aqueous suspensions of pulp will not be attempted. Electrolytic generation also offers problems. Instead, it is planned to generate superoxide from hydrogen peroxide by the horseradish peroxidase (HRP, EC1.11.1.7.) (45). Since the enzyme is effective over a limited pH range, ($\leq$7), the techniques will not give results directly comparable to commercial peroxidate bleaching technology.

Another approach which will probably give more significant results involves the bleaching of pulp in an alkaline peroxide solution containing reagents intended to suppress the concentration of hydroxyl radical. This technique allows one to decompose peroxide catalytically to a mixture of radicals.

$$Me_2SO + \cdot OH \rightarrow MeSO_2H + CH_3 \qquad (18)$$

$$\cdot CH_3 + (\cdot OH, O_2, \cdot O_2H, {}^{-}O_2H) \rightarrow \text{less reactive products}$$

As mentioned previously, DMSO and sodium formate react very rapidly with hydroxyl radical to minimize its effect during bleaching for DMSO. Sodium formate reacts as follows:

$$\cdot OH + H\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- \rightarrow \cdot\overset{\overset{O}{\|}}{C}\text{-}O^- + H_2O \qquad (19)$$

$$\cdot\overset{\overset{O}{\|}}{C}\text{-}O^- + \cdot OH \rightarrow HCO_3^- \qquad (20)$$

This reaction has been used with success by Bielski and Richter (46) to eliminate the effect of hydroxyl radicals in their studies while Mih (47) at the Institute has shown that DMSO (a known scavenger of hydroxyl radicals (1) inhibits the autoxidative degradation of lignin model compounds.

The degradation of the alkaline peroxide solution can be initiated by the presence of catalysts [for example, metals rather than salts would be employed in order to minimize metal ion catalyzed degradation of the fibers (48)] or better by heating or irradiating the solution until peroxide decomposition becomes appreciable.

The presence or absence of the various radicals in the peroxide solution can be verified by incorporating organic indicators. The use of these indicators will be discussed in greater detail later in this report. The presence of superoxide in similar reactions has frequently been detected by incorporating cytochrome C^{III} in the reaction mixture. Characteristic color changes and the suppression of some degradative actions might be anticipated as the oxidation of superoxide takes place (49). The likely sensitivity of this reagent to high pH

$$\text{cytochrome } C^{III} + \cdot O_2^- \rightarrow \text{cytochrome } C^{II} + O_2 \qquad k = 10^6 \text{ lmd}^{-1} \text{ sec}^{-1} \qquad (21)$$

levels makes it likely more sophisticated detectors will have to be used.

SINGLET OXYGEN EXPERIMENTS

The bleaching of pulp with singlet oxygen has many of the practical advantages and disadvantages associated with ozone bleaching. A summary of the chemical sources of singlet oxygen is given by Murray (49). These techniques include the classical peroxide-hypohalite systems, decomposition of organic peroxy acids, self decomposition of sec-butyl peroxy radicals and 1-phospha-2,8,9,-trioxaadamentane ozonide, base induced decomposition of peroxy-acetyl nitrate, decomposition of transition metal-oxygen complexes, decomposition of photoperoxides, the reaction of ozone with organic substrates, and the possible formation of singlet oxygen from the dismutation of superoxide anion in DMSO solution.

Some of these processes such as the decomposition of photoperoxides and the reaction of ozone with organic substrates are of current interest to the paper industry because of light instability of paper and degradations caused by ozone bleaching. The practical generation of singlet oxygen by chemical means would rely on the use of either the peroxide-hypohalite system and the decomposition of organic peroxy acids.

The bleaching of cotton has been achieved using the classical H_2O_2-NaOCl technique by a process involving unspecified catalysts and stabilizers (50). The use of this technique is not consistent with the ultimate goals of this project. Additionally, it is difficult to eliminate the possiblity that chlorine, hypochlorite or peroxide is really the effective bleaching chemical. Nevertheless, other researchers have shown both $^1\Delta g$ and $^1\Sigma_g^+$ states of oxygen are produced by the introduction of peroxide and chlorine with efficiencies of $^1\Delta g$ singlet oxygen production reaching 80%.

McKeown and Waters (51) have shown that singlet oxygen may be generated from organic peroxy acids maintained at their pKa values in yields up to 21%. More recently, Batsinali and Evans (52) have shown that monoperoxyphthalic acid at pH 8.2 can yield 60% singlet oxygen at room temperature. Some researchers have questioned the production of singlet oxygen from some peroxy acids and suggest instead a direct participation of the acid with the detecting reagents. The use of peroxy acids for singlet oxygen generation requires care, the yields must be improved, the acid must be recoverable, and the analysis of singlet oxygen production should be accompanied by several different confirmatory experiments (53).

It is felt that the chemical techniques for singlet oxygen generation are undesirable because of the complex disposal or recovery problem presented by the generating chemicals and because singlet oxygen has a very short halflife in aqueous media. Gaseous singlet oxygen has a relatively long lifetime (54) and can be reacted with pulp in a manner analogous to the use of ozone and thus presents a potentially useful alternative.

Gaseous singlet oxygen may be generated by electrical discharge in a "Woods tube" or more effectively by microwave discharge (55). The oxidant could presumably be reacted with high consistency pulp at ambient temperatures. Since a microwave discharge system was not available for experimentation, the chlorine-sodium peroxide technique of singlet oxygen generation was adapted for this purpose. A number of alternative processes were investigated but the most satisfactory to date involves passing a mixture of chlorine and nitrogen gases through a glass cylinder containing sodium peroxide. On top of the peroxide is a layer of crushed ice which is separated by a 2-cm pad of glass wool from the pulp to be bleached. The rate of flow of gas must be slow enough that the peroxide does not ignite, and fast enough that the singlet oxygen will not decompose before reaching the pulp.

A rate of flow slower than that rate which produces a red glow of decomposing singlet oxygen in the tube has been found to be most satisfactory. A schematic outline of the device is shown in Fig. 57.

In theory, there should be no opportunity for any oxidant except oxygen, chlorine and singlet oxygen to come into contact with the pulp, and this goal was often achieved. The best bleaching results were obtained when the foam from decomposing peroxide reached the lower edge of the pulp. It could be argued that oxidants other than singlet oxygen were participating. The bleaching action was limited to the outer surfaces of the clumps of kraft pulp. After reaction was complete (a few seconds to 3 1/2 minutes), the pulp was divided into bleached and unbleached components and subjected to limited analysis. Some initial small scale bleaches gave fractions achieving 80 GE brightness after less than a minute reaction. A larger bleach involving 17 grams of pulp was divided into 3 degrees of bleaching, and the analyses are given in Table VI.

A portion of the pulp (16%) was bleached in 3 1/2 minutes to a high level of brightness which was unchanged by subsequent washing and isolation. The brightness of 69 represents the average of a wide range of brightnesses. The brightness could be improved greatly by reductions with $NaBH_4$. Although control experiments using chlorine gas and peroxide independently caused little change in pulp brightness, the possibility of a bleaching action by HOCl is not yet ruled out. It is planned to repeat the bleaching with pulp containing chemicals susceptible only to the action of singlet oxygen.

Although the pulp was bleached to a significant level, the breaking length of handsheets prepared from the pulps decreased to a value of about half of that of the unbleached pulp as the brightness increased. SEM examination

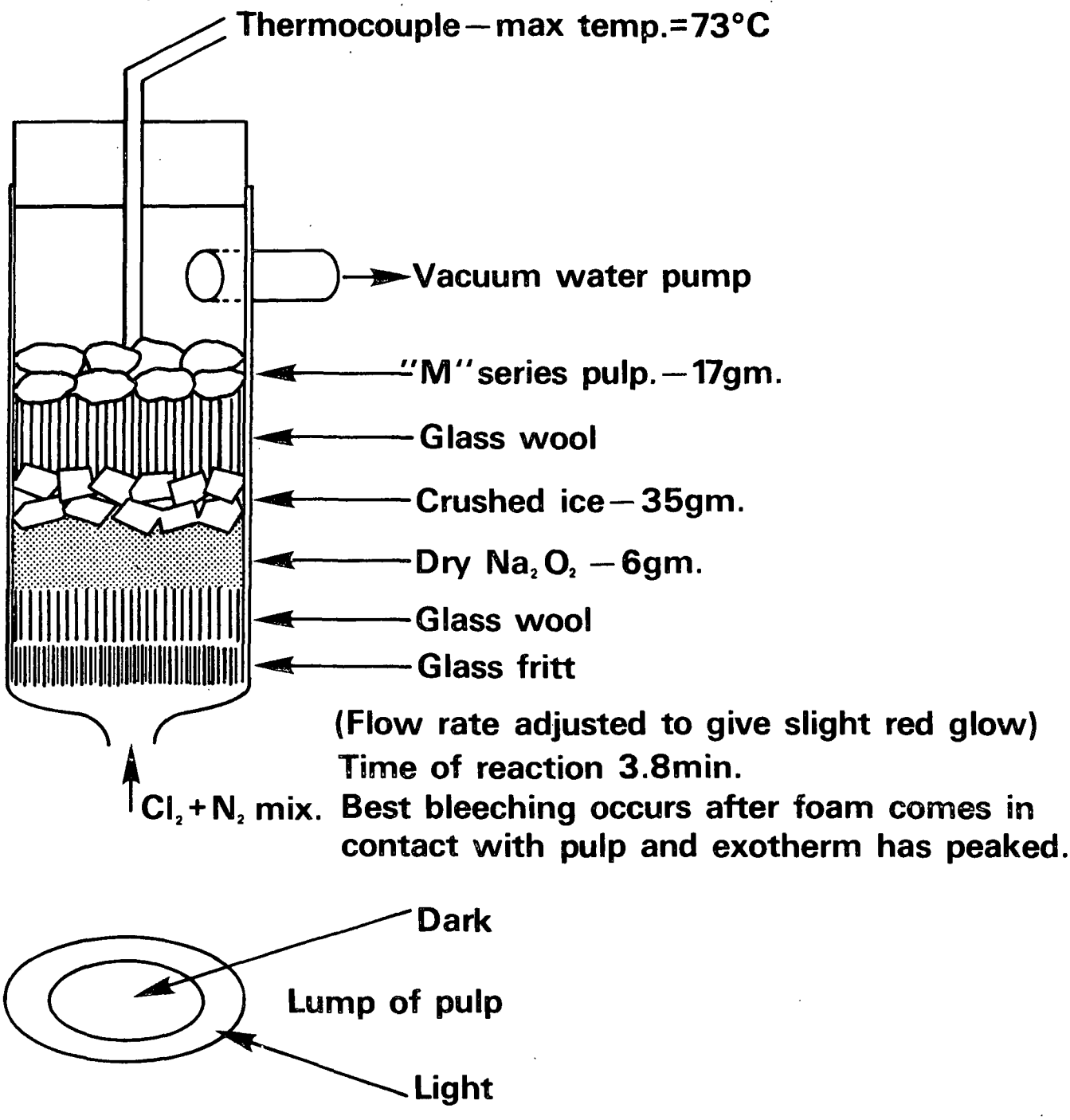


Figure 57. Apparatus for Reacting Pulp with Singlet Oxygen

indicated very few cleaved tracheids were present (Fig. 58), and the surface texture indicated a slight exposure of the underlying microfibrils of the outer wall (Fig. 59). The tracheids did exhibit a peculiar localized type of erosion (Fig. 60) in which the distortion spots characteristic of broken fibrils are evident. On the basis of this observation, it is conjectured that considerable cleavage of fibrils and microfibrils of the secondary wall has also occurred and that this phenomenon is responsible for the poor breaking length characteristics of the "singlet oxygen" bleached pulp. It is possible that the observation of the effect of singlet oxygen on the surface of the tracheids might be improved if the reacted pulp was subjected to a mild delignification before SEM examination.

TABLE VI

THE PROPERTIES OF PULPS BLEACHED WITH SINGLET OXYGEN

		Bleached Pulp Mechanically Separated According to GE Brightness		
Yield, %	Control	54	15	16
Brightness, GE	23.8	39.9	57.6	69.1
Brightness, GE (after aging)	23.7	28.6	54.3	59.0
Breaking length, km	14.1	11.2	8.9	7.8

DISCUSSION AND SUMMARY

Techniques and reagents are available to investigate the effects of superoxide in aqueous medium on the degradation of pulp, and experiments will be carried out in the immediate future. In addition, attempts have been made to improve bleaching pulp with gaseous singlet oxygen. Experiments are planned to determine if singlet oxygen was responsible for the bleaching action as well as the degradation which has been observed to occur at the same time. If these investigations show that singlet oxygen is indeed the reactive species, and if pulp

degradation can be kept under control, it is planned to consider the trial use of singlet oxygen produced by microwave radiation.

Figure 58. Southern Pine Kraft Pulp, 30 Kappa, Reacted with Singlet Oxygen, #5042, 300X

Figure 59. Southern Pine Kraft Pulp, 30 Kappa, Reacted with Singlet Oxygen, #5044, 5000X

Figure 60. Southern Pine Kraft Pulp, 30 Kappa, Reacted with Singlet Oxygen, #5043, 5000X

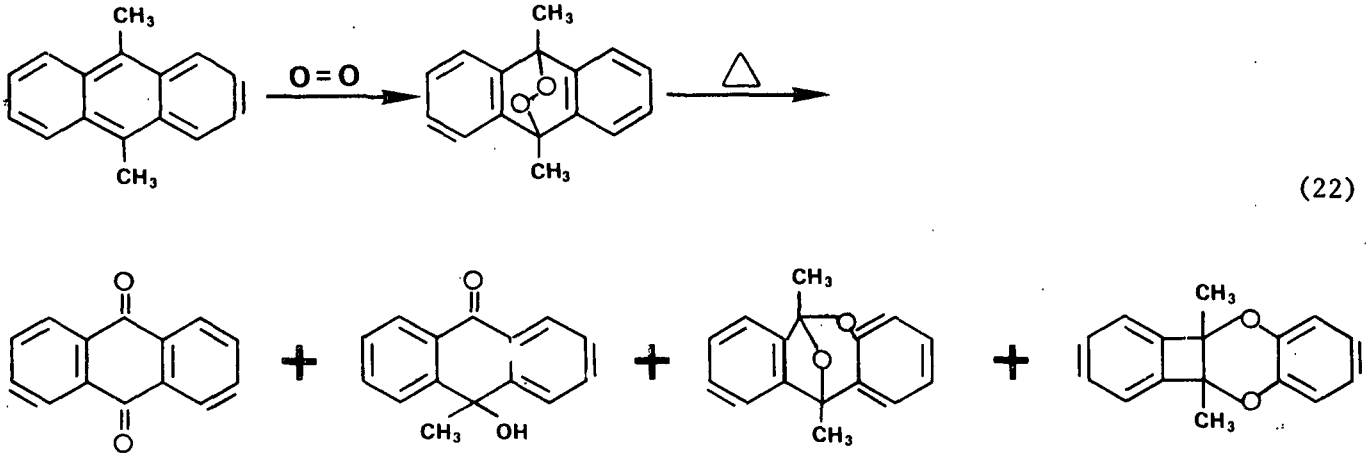
DETECTION OF OXYGEN RADICALS DURING BLEACHING

INTRODUCTION

As the foregoing discussions have indicated, the nature of many of the degradative participants during oxygen and peroxide, as well as ozone, singlet oxygen, and even peroxy acid, bleaching is not well understood (56). Considerable literature exists describing the use of chemicals specific to various radicals (because of their importance to biological processes). Many are not as specific as has been claimed but it does appear likely that at least some of them will react in specific ways with hydroxyl radical and singlet oxygen. It is proposed to follow the interactions of the detecting agents with radicals by quantitative GLC (how much has reacted) and by GLC-MS in order to ascertain from product identification how much each radical species has contributed to the destruction of the detecting agent.

A review of the many possibilities in the literature has led to a consideration of the reagents in Table VII for use in detecting radicals. Those marked with an asterisk have undergone preliminary examinations and have been reacted with KO_2. Some additives such as DMSO and sodium formate do not give characteristic degradation products. Their effects will have to be inferred from other evidence such as the quality of bleached pulp resulting after their incorporation into the bleach.

The presence of the low energy form of singlet oxygen can be detected by a wide variety of reagents. The reaction usually depends upon a 1-4 addition across a dienone configuration as illustrated for 9,10-dimethyl anthracene.



(22)

TABLE VII

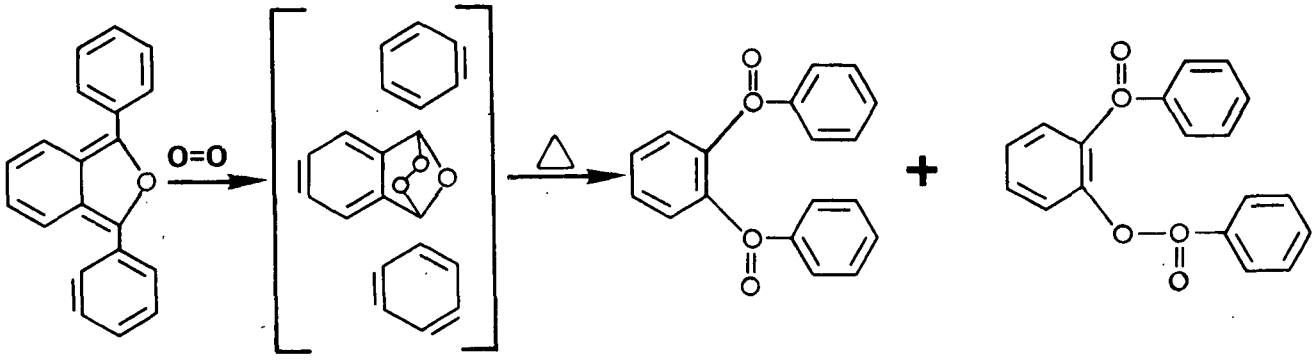
REAGENTS USED FOR THE DETECTION OF OXYGENATED RADICALS

Reagent	Test For $\cdot O_2H$	Test For $\cdot OH$	Test For $O = O$	Reference
Anthracene			+	60,61
9,10-diphenyl anthracene			+	51,61
9-methyl, 10-phenyl anthracene			+	51
9,10-dimethyl anthracene[a]			+	51,61
Anthracene, 9,10-bisethane sulfonic acid			+	52
Tetramethyl ethylene			+	57,59,61,67
1,3-diphenylisobenzofuran[a]			+	58,61
1,2-dimethyl cyclohexane			+	58
2,5-dimethylfuran			+	58,65,67
Tetraphenylcyclopentadienone[a]	+		+	59,66,67
4-(N-methylpyridinium) t-butyl nitrone		+		64
5,5'-dimethyl-1-pyrroline-1-oxide		+		64
Alkyl sulfoxides		+		35

[a]Reagents under active consideration.

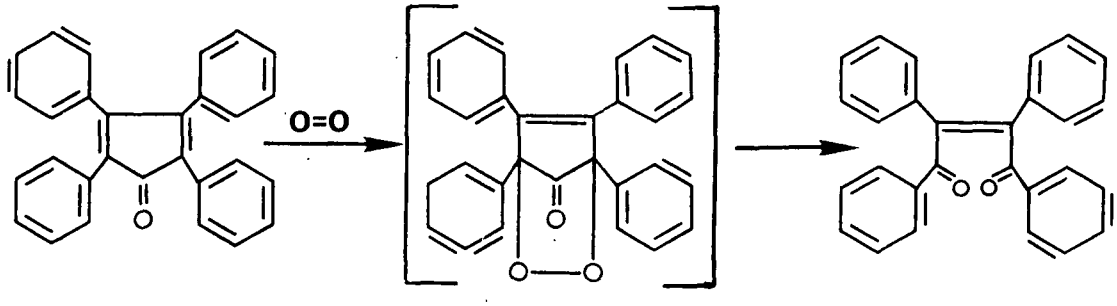
The change in concentration of the test reagent is usually measured by spectrophotometric means. It is proposed to confirm the radical oxidation by GLC-MS. Even this confirmatory analysis must be treated with care because the reaction products may themselves react further during the relatively severe bleaching conditions as suggested above.

In a similar manner, 1,3-diphenylisobenzofuran gives a single product when reacted with singlet oxygen under mild conditions. Control experiments will have to be undertaken to determine the stability of this product under bleaching conditions.



(23)

Tetraphenylcyclopentadienone is known to react with both superoxide and singlet oxygen to give different products. The proportion of these two intermediates in a bleaching process can be determined by GLC-MS techniques, and the effect of the treatment on the desired reaction product can be ascertained by proper control experiments. The reaction with singlet oxygen is as follows:



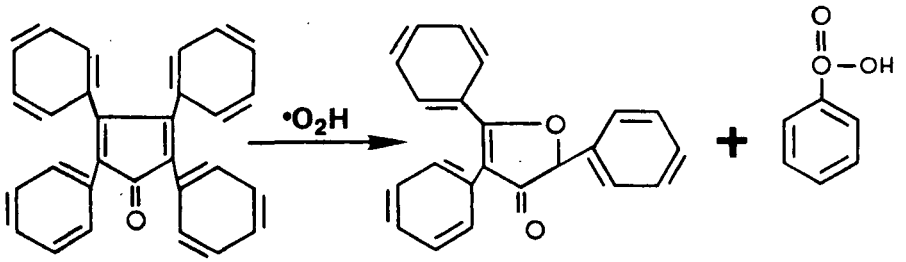
(24)

Initial experiments have shown that all three indicator substances can be separated by GLC. A complicating result indicated 1,3-diphenyliso-benzofuran slowly reacts with DMSO to form an oxidized derivative. Alternative solvents such as pyridine can be employed to eliminate that side reaction. Other experiments indicated the use of DMSO as solvent complicates the interpretation of GLC-MS spectra. Chloroform was found to be an alternative solvent for use with the GLC.

Each of the reagents was reacted with KO_2 in DMSO to test the accuracy of the response data reported in the literature. 9,10-Dimethyl anthracene and 1,3-diphenylisobenzofuran, which are both reportedly stable to $\cdot O_2$ or KO_2, do react slowly with that oxidant. Two additional responses were observed from the anthracene derivative after prolonged treatment with KO_2 at room temperature. 1,3-Diphenylisobenzofuran showed 4 additional responses on the GLC in addition to the two responses caused by reaction directly with DMSO. It is hoped GLC-MS interpretation of these results will indicate whether there is a slow degradation of KO_2 to singlet oxygen (as claimed by Kahn (69) and rejected by others (70,71) or if the reaction reflects other chemical effects of superoxide.

The reactivity of pulps with KO_2 in pyridine compared to DMSO solvent suggested the complications conjectured by Kahn (69) did not occur in the previous research. Nevertheless, the possibility for this reaction does exist because Kahn subsequently showed by a theoretical analysis that the production of singlet oxygen from ion clusters of superoxidate is critically dependent upon the number of water molecules present (72). Beyond this narrow range, singlet oxygen can be efficiently quenched by superoxide. This quenching action has been reported several times in the literature.

Tetraphenylcyclopentadioxone reacted very quickly with KO_2, as evidenced by the disappearance of a colored solution, and GLC analysis of the oxidation products revealed no starting material and two relatively volatile fragments whose existance is consistent with the known behavior of that reactant to KO_2. The reactions proceed as follows:



(25)

DISCUSSION AND SUMMARY

The use of reagents for detecting various radical and reaction species derived from oxygen is critical for the success of this project. It is important to understand the conditions necessary for the generation or elimination of radical intermediates in order to plan techniques to make these substances useful in bleaching.

The compounds under consideration will, according to the literature, react more or less specifically with superoxide, hydroxyl radical, and singlet oxygen. The truth of these observations will be verified as far as possible within the constraints of the project. Since some reagents will react with many radicals by characteristic mechanisms extensive use will be made of the GLC-MS for unravelling that complication.

It is planned to sorb suitable radical indicators onto pulp and remove the carrying solvent. The pulp will then be bleached by a suitable technique

and the indicator and its indication products will be removed (by suitable extracter techniques) and analyzed by quantitative GLC and GLC-MS. With suitable controls this technique will show the presence of radical participants and the contribution of each to pulp characteristics.

ACKNOWLEDGMENTS

The authors appreciate the assistance of John Litvay, Walter Rantanen, Hilkka Kaustinen and Mary Block for SEM photographs and fiber length distributions. Leroy Borchardt, Bette Wabers and Leo Schroeder are thanked for lignin and carbohydrate analysis and HPLC examination of cotton.

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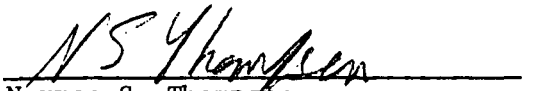

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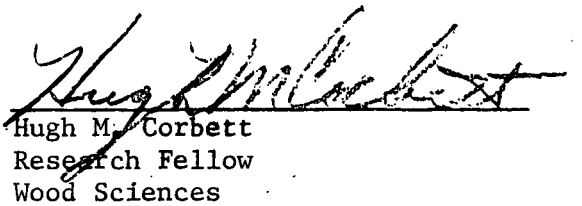

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APPENDIX I

THE CHANGE IN DEGREE OF POLYMERIZATION OF COTTON STAPLE WITH TIME OF REACTION WHEN REACTED WITH KO_2 IN DMSO

Sample	Degree of Polymerization from HPLC: At Maximum of Distribution Curve	Number Average	Viscosity[a]	Weight Average	Cuene Viscosity[b]: cps	D.P.
Control	7750	1011	6704	6992	186	--
1 hour reaction	525	295	840	878	3.10	420
2 hour reaction	356	237	541	561	2.35	350
3 hour reaction	317	245	545	564	1.80	280
4 hour reaction	294	213	471	486	1.88	290
5 hour reaction	193	164	313	322	1.73	270
6 hour reaction	186	170	324	333	1.74	270
Soluble cellulose component	140	125	186	190	--	--

[a] DP from HPLC measurements

[b] 0.5% Cuene solution; Tappi T230; DP estimated values from Tappi data sheet 113 C (December, 1950).